A THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

THE THERMAL DECOMPOSITION OF SOME POLY(METHYLPHENYLSILOXANES)

BY

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PREFACE

The work described in this thesis was carried out by the author at the University of Glasgow, in the Department of Physical Chemistry, which is under the supervision of Professor G A Sim.

I should like to express my sincere gratitude to my supervisor Professor N Grassie for suggesting the topic of this thesis and for his interest, encouragement and advice throughout the course of this work.

I acknowledge the assistance given by my colleagues in the Macromolecular Chemistry Group for their helpful discussion, suggestions and good humour. In particular, my thanks go to Dr Ian Macfarlane and Miss Sheila Beattie BSc for their help with the work described in Chapter 3 and 7, respectively. To the various members of the Departmental tecnical staff, especially Mr J Gorman and Mr G McCulloch, I also extend my thanks.

I am grateful to the Science Research Council for the award of a grant during the tenure of which this work was carried out.

Finally, I thank my wife, Jennifer, for typing the manuscript and for her patience and understanding during the period of this work.

Kenneth F Francey

SUMMARY

The demand for materials with high thermal and oxidative stability increases with the technological advances made by industry. Silicones have found extensive use as thermally stable oils, rubbers and resins since their introduction in the early forties. In recent years, research has been carried out to relate fundamental knowledge of polymeric reactions to their physical behaviour under working conditions in order to improve their properties. This work is aimed at increasing the understanding of the thermal breakdown of some linear polysiloxanes with methyl and phenyl side groups.

A comprehensive review of the literature relating to the degradation of polysiloxanes is given in Chapter 1 along with brief notes on their history, uses and nomenclature.

A list of the chemicals used and polymerisation techniques is given in Chapter2 along with details of the apparatus and experimental techniques employed in this study. Notes on thermal analysis techniques and techniques for qualitative and quantitative analyses of products are also given in this Chapter.

The preparation and thermal degradation of poly(methyl/phenylsiloxane) is discussed in Chapter 3. The main products are cyclic trimer, tetramer and pentamer isomers. Benzene is also formed.

In Chapter 4, the preparation and thermal properties of a series of poly(dimethyl/methylphenylsiloxane) copolymers is described. Twenty six different cyclic

compounds, from trimer to hexamer, have been identified in the degradation products along with small amounts of benzene.

A series of poly(dimethyldiphenylsiloxane) copolymers has been prepared and their thermal degradation under vacuum has been studied. Over twenty different cyclic siloxanes have been separated from the degradation products and the results are described in Chapter 5. Benzene is again a product.

The results from Chapters 3,4 and 5 are summarised in Chapter 6 and the stability of the three systems is compared.

In Chapter 7, preliminary studies on block copolymers of poly(siloxane-urethane) are described. There is evidence that these copolymers depolymerise by a similar mechanism to organic polyurethanes with the formation of urea and carbodiimide structures. Carbon dioxide and benzene are present in the volatile products of degradation.

C O N T E N T S

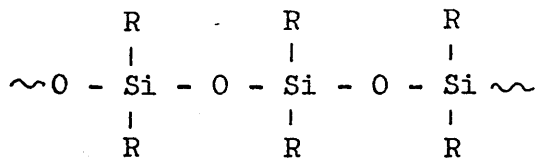
CHAPTER 1

1.1 General Introduction (Refs: 1-9)

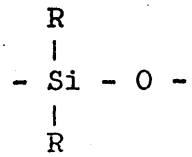
In an effort to produce polymers with radically different properties to those of the wholly organic polymers, a great deal of research has been based on attempts to incorporate elements other than carbon, nitrogen, oxygen, sulphur and the halogens, into the polymer chain. Silicon was the first element to be used successfully to synthesise novel macromolecules of this type (Ref: 1). When these polymer chains - made entirely of silicon - proved unstable, attention then switched to polymers containing alternate silicon and oxygen atoms, with organic substituents on the silicon atoms. Thus, in 1939, Andrianov (Ref: 2) was the first to prepare the new class of organosilicon polymers, now known as polyorganosiloxanes or silicones.

Polysiloxanes can be represented by the general formula $\left[(R_a . SiO_{4-a})\right]_n$, where "n" is large and "a" varies between 0 and 4.

When a = 2 this formula represents linear polysiloxane:

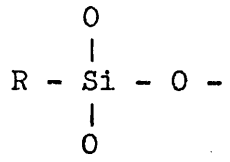


when a = 3 the monofunctional species:



and when a = 1

the trifunctional species:



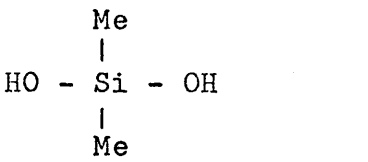
Since the early forties a vast industry based on silicones has been developed to meet the technological demands of an everchanging world. Properties which make silicones important include: resistance to moisture, heat, cold, UV and other radiation, oxygen and ozone, small temperature dependence of viscosity and modulus of elasticity, and their high dielectric properties. These properties can be manipulated by changing the type of organic radicals on the silicon atoms, the molecular weight of the polymer, the degree of cross-linking and by the addition of fillers such as Carbon Black.

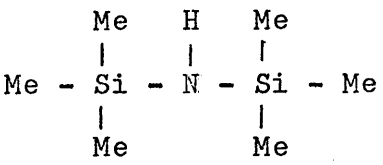
It has been shown that for maximum resistance to heat, a radical which does not unsaturate gives the most stable polymer. Many organic radicals have been studied in an attempt to produce more stable polymers, but methyl and phenyl groups continue to be the most widely used. The introduction of hetero-atoms such as titanium, tin, aluminium, boron and phosphorus (Ref: 3) into the siloxane backbone has been investigated and polymers with improved thermal properties have been prepared in this way. Pure polysiloxanes, however, remain more economically viable for general commercial purposes.

1.2 Nomenclature

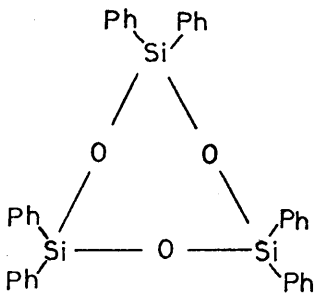
The nomenclature, used in this thesis, for the simpler organosilicon compounds will be according to the rules laid down by IUPAC (ref: 10).

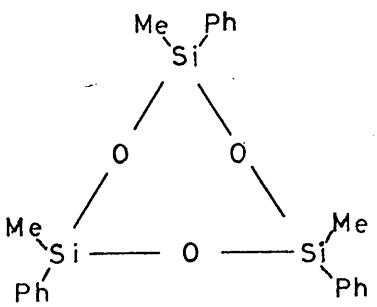
For example,





Dimethylsilane diol 1,1,1,3,3,3, hexamethyldisilazane





Hexaphenylcyclotrisiloxane 1,3,5, trimethyl, 1,3,5, triphenylcyclotrisiloxane

It is sometimes more convenient to represent siloxanes by the'shorthand' method first proposed by Hurd (Ref: 11). This method describes the functionality of the monomer units by letters;

M - Monofunctional $R_3 SiO$

D - Difunctional $R_2 SiO_2$

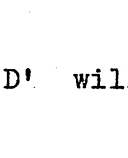
T - Trifunctional $R SiO_3$

Q - Quadrifunctional SiO_4

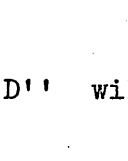
where R normally represents a methyl radical

In this thesis, difunctional units which have one or two phenyl units on the silicon will be represented as follows:

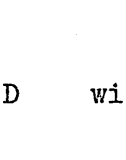
D' will represent



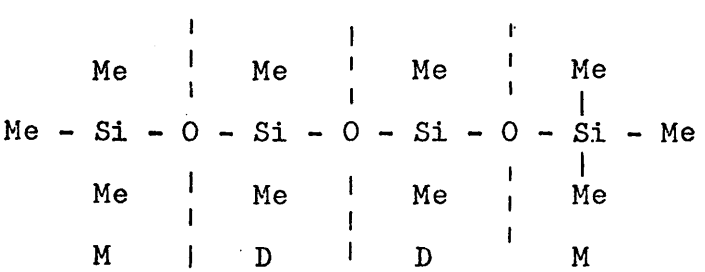
D'' will represent



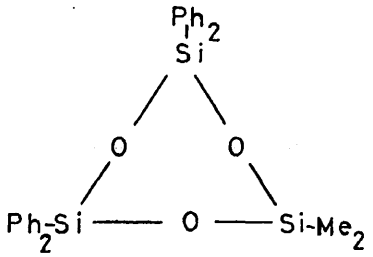
D will represent



To illustrate this system, the linear molecule decamethyltetrasiloxane,

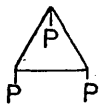


would be written simply as MD_2M and the cyclic molecule 1,1,dimethyl, 3,3,5,5, tetraphenylcyclotrisiloxane

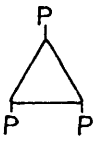


would be D_1D_2''.

The geometric isomers of certain cyclic siloxanes are often more easily distinguished by the following abbreviated structural representations:



cis 1,3,5,trimethyl, 1,3,5, triphenylcyclotrisiloxane



trans 1,3,5,trimethyl, 1,3,5,triphenylcyclotrisiloxane

For clarity, only the phenyl radicals are shown, with methyl groups occupying the unfilled valencies.

1.3 Polymer Degradation (General) Refs: 12-15)

(i) Introduction

The term polymer degradation is used to describe any reaction undergone by the polymer whether or not it results in the deterioration of any of its properties. Polymers are subjected to a variety of degradative influences, both in their fabrication and in their everyday usage.

These influences include the action of heat, oxygen, mechanical stress, chemicals, bacteria and light (and other radiation), and they may act together or separately depending on the environment and application of the polymeric material. To study the simultaneous effects of more than one of these influences is usually quite difficult. Hence most research has involved the study of only one variable under closely controlled conditions.

The data from degradation studies can be used to explain the behaviour of polymers under extreme conditions and can lead to methods of stabilising - or de-stabilising- the polymers once the degradation mechanism has been elucidated.

In this way, polymers with,say, high thermal stability can be prepared or, if required, with low stability under specific conditions, for example, 'bio-degradable' plastic wrappings or marine anti-fouling paints which hydrolyse, releasing toxic agents.

Such studies also give insight into the micromolecular structure of the polymer providing information about the arrangement and sequence of repeat units, side groups and possible 'weak links' in the polymer chain as well as giving details about chain-ends and cross-links between the chains. The kinetics of degradation reactions and the effects of varying sample environment on the products and rates of degradation can also be studied.

(ii) Mechanisms of thermal degradation

The mechanisms of thermal degradation fall into two distinct categories:

a) Chain-scission reactions

b) Substituent reactions

Chain-scission reactions involve the rupture of the macromolecular chain to form products similar to the starting polymer, that is, the products still contain the same repeat units as the polymer. New types of end groups may or may not appear depending on the nature of the chain-scission reaction.

Substituent reactions involve the rearrangement and/or elimination of the side groups in the main chain without rupture of the polymer backbone and thus change the chemical nature of the repeat units. Any volatile products formed are chemically unlike monomer.

1.4 Thermal Degradation of Linear Polysiloxanes

As with other commercially important branches of science, there is a vast amount of literature on Polysiloxanes. A great deal of the work has been carried out by industrially orientated research workers whose data sometimes have to be viewed with caution. Often, commercial samples of questionable purity are studied and exaggerated, and even false claims are not uncommon. Hunter (Ref: 6), for example, quotes a US patent which claimed to have studied approximately 10^5 compounds.

(i) Products of degradation

Polydimethylsiloxanes (PDMS)

Patnode and Wilcock (Ref: 16), in 1946, were first to give details of the thermal degradation products from linear PDMS. On heating (under nitrogen) up to 350°C, they observed the production of small amounts of water and cyclic siloxanes. On raising the temperature to 400°C, the sample decomposed completely to give the following yields of cyclic products:

D_3	44%
D_4	24%
D_5	9%
D_6	10%
Above D_6	13%

These results show that thermal decomposition of PDMS involves the scission of the Si-O bond.

Alexsandrova et al (Ref: 17) found the degradation products of commercial samples of PDMS at 400°C, under vacuum, to consist of a mixture of D_3 and D_4 with small amounts of D_5, D_6 and D_7. Methane and hydrogen were also identified suggesting that rupture of Si-C bonds, as well as Si-O bonds, was occurring. Andrianov et al (Ref: 18) also observed methane formation from hydroxy ended PDMS but not from trimethylsilyl end-blocked samples.

In 1969, Thomas and Kendrick (Ref: 19) reported the following yields of products (weight %) from the decomposit/ion of trimethylsilyl end-blocked PDMS:

D_3	43.7
D_4	23.5
D_5	9.7
D_6	10.9
D_7	7.2
D_{8-12}	5.0
MM	0.3
MDM	1.0

After heating at 420°C for five hours, the sample had completely decomposed with no evidence of any Si-C bond rupture.

More recently, Macfarlane (Ref: 20) has found the following weight per cent yields in the thermal degradation products of hydroxy ended PDMS:

	275°C	300°C	335°C	385°C	405°C
D_3	69	78	74	70	60
D_4	14	12	12	11	11
D_5	5	5	4	2	6
D_6	7	3	4	7	12
D_7 upwards	5	2	6	10	11

He found no evidence of Si-C bond scission (i.e. no methane production) from either end-blocked or hydroxy ended samples and every polymer degraded quantitatively to volatile products whether it was degraded under vacuum or under nitrogen. Macfarlane did observe methane pro/ duction and extensive cross-linking, however, when samples were contaminated with small amounts of KOH.

Methyl and phenyl polysiloxanes

Thomas and Kendrick (Ref: 21) degraded a sample of end-blocked polymethylphenylsiloxane at 400°C (under nitrogen) and obtained trans D_3' and D_4' isomers as the products. They saw no evidence of Si-C bond scission.

Macfarlane (Ref: 20) has degraded samples of poly/ dimethyldiphenylsiloxane prepared by copolymerising D_4 and D_4'' - and has found the decomposition products to consist of dimethyl and 'mixed' dimethyldiphenyl cyclic

siloxanes. He also observed the evolution of small amounts of benzene and trace amounts of 'non-condensable volatiles' from these copolymers, inferring that rupture of Si-C bonds was occurring.

(ii) Thermal decomposition mechanisms

The literature describes three main reactions undergone by PDMS on heating i.e.

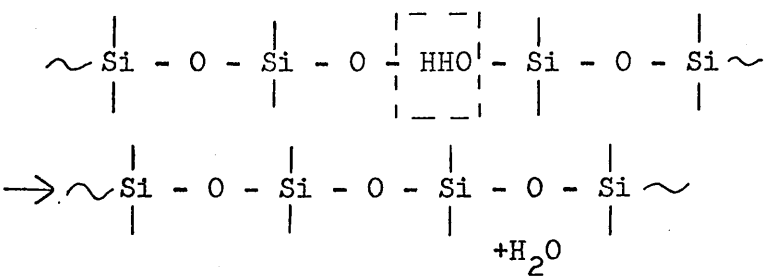
a) Condensation of terminal hydroxy groups (Refs: 16, 20, 22)

b) Production of cyclics (Refs: 17-20, 22-25)

c) Production of methane (Refs: 17, 18, 20)

Polycondensation of terminal hydroxy groups

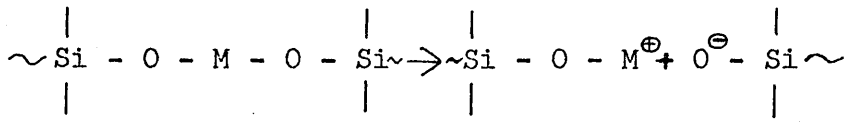
This reaction occurs before any weight loss from the polymer is observed (Ref: 20, 22) and is manifested by a rise in the intrinsic viscosity of hydroxy ended PDMS caused by an increase in molecular weight, thus:



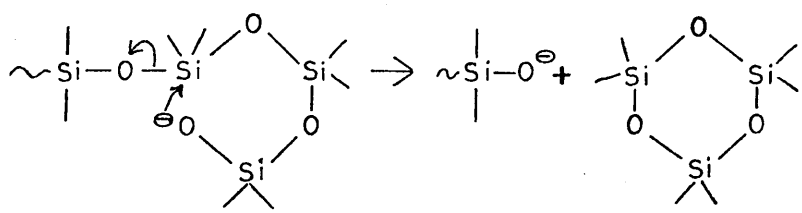
Only Patnode and Wilcock (Ref: 16) found water in the products of degradation however.

Production of cyclics

Lewis (Refs: 23, 24) proposed that the depolymerisation of PDMS was catalysed by impurity atoms incorporated in the backbone of the siloxane chain. Analysis of his samples by emission spectroscopy revealed the following metallic impurities: barium (0.05%), lead (0.01%), aluminium (0.005%), magnesium (0.001%) and silver (0.0005%). The polymer molecules were thought to dissociate at the sites of the impurity atoms (M)

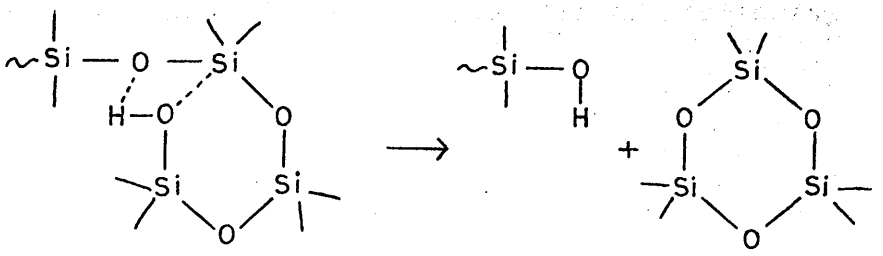


to give ionic end groups which would then cause depolymerisation giving low molecular weight cycles. Thus:



Lewis attributed the lack of reproducibility in the degradation behaviour of his samples to chain cleavage catalysed by trace impurities.

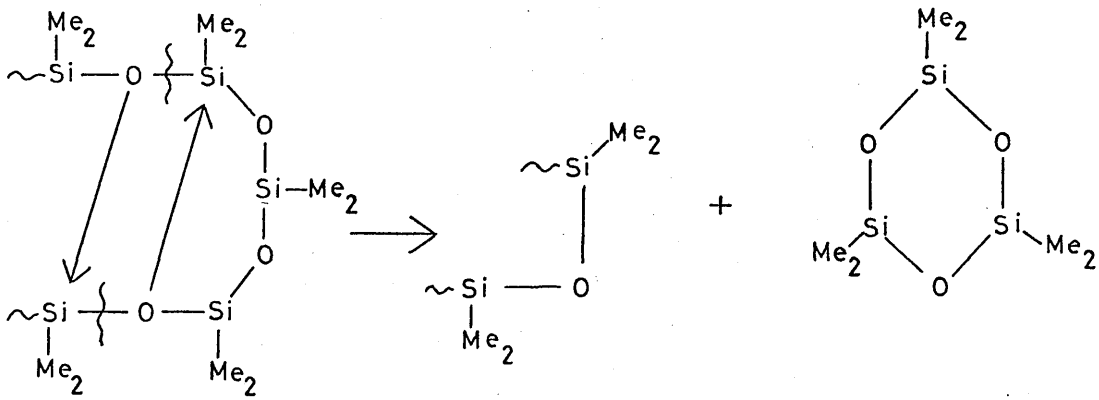
Alexsandrova et al (Ref: 17) showed that the rate of depolymerisation depended on chain end groups and proposed the following mechanisms for the formation of cyclics:



Rode et al (Ref: 22) put forward a similar mechanism, suggesting that the large mobility of the siloxane chains and their spiral structure would cause ring closure via the formation of an intermediate transition complex with excited Si-O and O-H bonds. They predicted an activation energy of 14 k cal mol^{-1} for this reaction and claimed experimental results gave good agreement. They also showed that polymer samples with chain ends capped with trimethyl silyl groups were more stable, as was predicted. Andrianov et al (Ref: 18), while agreeing in principle with the mechanism proposed by Rode et al (Ref: 22), have suggested that depolymerisation in the latters' samples was due to residual catalyst (sulphuric acid).

Thomas and Kendrick (Ref: 19) have offered an alternative mechanistic approach to the depolymerisation of PDMS. Using trimethyl silyl end-blocked samples, they studied the thermogravimetric behaviour of catalyst-free polymers under vacuum and in an atmosphere of dry argon andfound an activation energy of depolymerisation of 42 ± 3 k cal mol^{-1}. They postulated the formation of an intramolecular four-centred transition state-using silicon d orbitals -

which leads to the expulsion of a cyclic molecule by rearrangement of siloxane bonds in the following manner:



They claim the formation of the transition state could have an activation energy of about 40 k cal mol^{-1} and it could be formed at any point along the chain. Thus the process would proceed until the chain was too short to cyclise readily.

Sobolevskii et al (Ref: 25) have studied the composition of pyrolysis products for dimethyl cyclic and linear oligomers. They proposed that the oligomers undergo rearrangement via the homolytic fission of Si-O bonds. The radicals so formed can then react to give the various cyclic and linear species identified in the products.

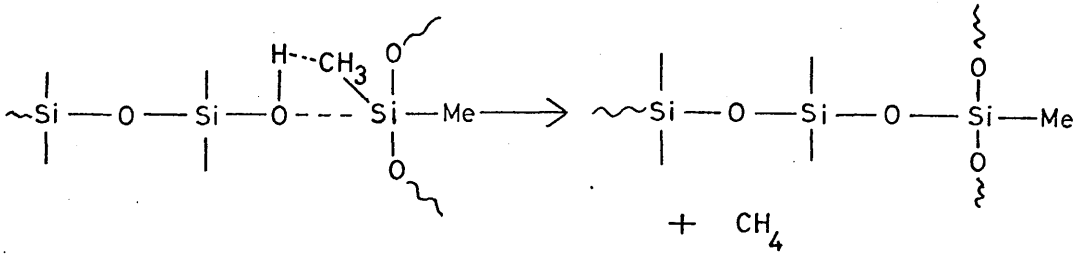
More recently, Nielson (Ref: 26) has proposed that PDMS undergoes rapid inter - and intra - molecular rearrangements above 375°C by a mechanism similar to that described by Thomas and Kendrick (Ref:19). Nielson states

that the Si-O bond has no 'thermal integrity' at higher temperatures. Macfarlane (Ref: 20), however, failed to find any evidence of intermolecular rearrangement when he degraded a blend of PDMS and polymethylphenylsiloxane. If intermolecular reactions were occurring, degradation of the above blend should give cyclic products containing dimethyl and methylphenyl units. Macfarlane, however, identified only dimethyl and methylphenyl cyclics in the products.

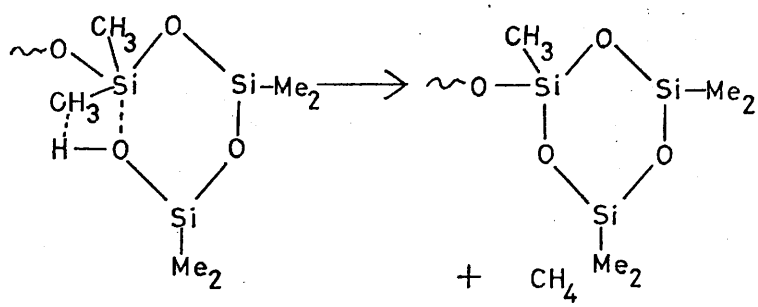
Production of methane

The evolution of methane from PDMS has been observed by some workers (Refs: 17, 18) but not by others (Refs: 19, 20, 22-26).

Andrianov et al (Ref: 18) observed methane evolution above 350°C with loss of sample solubility and postulated a reaction mechanism involving hydroxy chain ends.

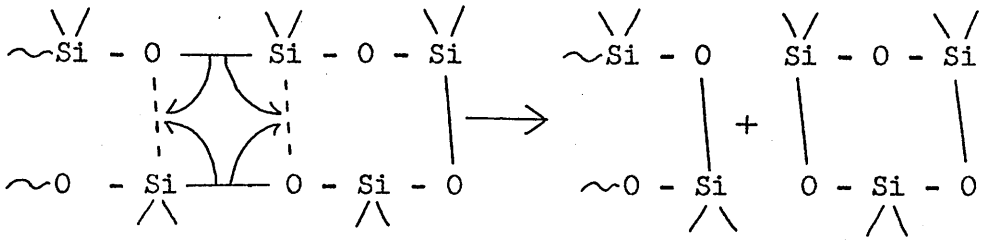


Alexsandrova et al (Ref:17) observed Si-C bond scission in PDMS but without loss of sample solubility. They proposed the following intramolecular reaction to account for the formation of small amounts of methane:



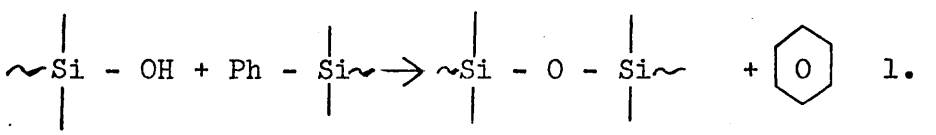
Macfarlane (Ref:20) only observed methane as a decomposition product when PDMS was contaminated with KOH and he suggested that the evolution of methane observed by the above workers was due to the presence of impurities.

Thomas and Kendrick (Ref: 21) have studied the decomposition of polymethylphenylsiloxane (PMPS) with trimethyl silyl end groups and have proposed a mechanism of depolymerisation similar to that for PDMS (Ref: 19). They claim that electron donating groups on the silicon atoms would tend to increase the electron availability of the oxygen atoms, thereby facilitating the formation of the transition state and thus lowering the activation energy of depolymerisation.



The activation of energy for PMPS was found to be higher than predicted and they have suggested this was due to silicon d orbital participation in π electron system of the phenyl group which they claim becomes electronically equivalent to a methyl group when attached to a silicon atom.

Chubarov et al (Ref: 27) have studied the thermal degradation properties of cross-linked methyl and phenyl polysiloxanes and have observed the evolution of benzene (at 550°C-600°C), and methane and hydrogen (at 750°C - 800°C) from their samples. They have postulated the following mechanisms to account for this:



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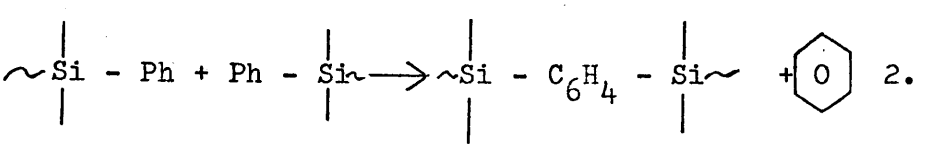

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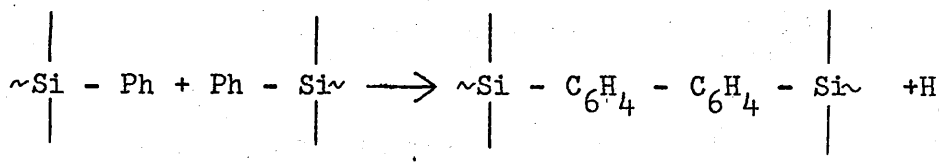

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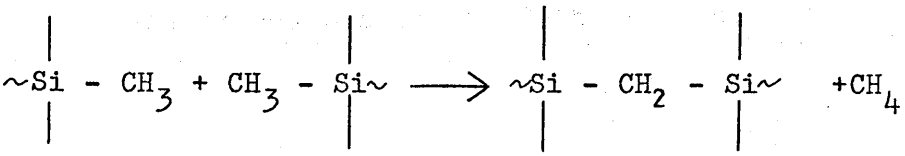
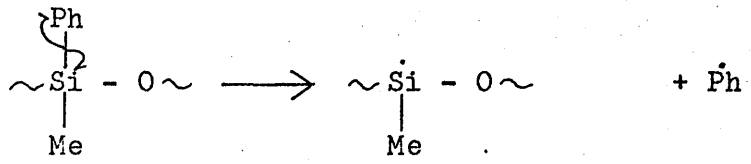
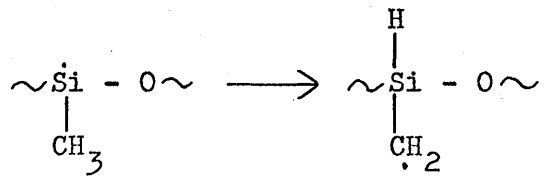


4.

Finally, Sobolevskii et al (Ref: 28) have studied thermally induced changes in oligomethylphenylsiloxanes. Between 425°C and 475°C, they found that the oligomers underwent rearrangement to form a variety of linear and cyclic siloxanes. At higher temperatures (475°C - 500°C), Si-C bond scission occurs leading to the formation of insoluble polymers. They have proposed that the first reaction involves homolytic fission of Si-O bonds followed by rearrangement and recombination of the radicals. For the second reaction, rupture of Si-Ph bonds is proposed:



followed by rearrangement of the radicals:



(iii) Effect of residual catalyst on thermal stability

Lewis (Ref: 24) and other workers (Ref: 20, 29) have shown that residual catalyst drastically lowers the thermal stability of polysiloxanes. It is vital, therefore, that all traces of catalyst are removed from the polymer if it is to be studied scientifically.

Three approaches to this problem have been suggested:

a) neutralisation of residual catalyst (Ref: 30)

b) extraction of catalyst by water (Ref: 31)

c) use of transient catalysts (Ref: 32)

The first two are unsatisfactory since complete removal of all catalyst will be impossible from high molecular weight samples.

The transient catalyst tetramethyl ammonium hydroxide (TMAH) has been used for all polysiloxane polymer/ isations carried out in this work. TMAH rapidly decomposes at 130°C to form methanol and trimethylamine, neither of which react with the polymer (Refs: 3, 32).

(iv) Effects of structure on thermal stability

Andrianov (Refs: 33, 34) has suggested that the spiral structure of linear polysiloxanes creates favourable conditions for the formation of cyclics. Enlarging the organic radical on the silicon atoms will hinder spiral formation and so lower the rate of depolymerisation - polydiethylsiloxane decomposes at higher temperatures than PDMS(Ref: 34). Polymers with three dimensional structures have greater thermal stability than linear polymers due to the lower mobility of the chains which are thus less able to form spiral structures, and because depolymerisation necessitates the rupture of two or three bonds, whereas linear polymers need only cleave one bond.

The enhanced stability of polysiloxanes with phenyl in place of methyl groups has been explained by the screening effect of the phenyl groups on the siloxane backbone (Ref: 35) and by the electron withdrawing effect of the phenyl group strengthening the Si-O bond (Ref: 36).

Sobolevskii et al (Ref: 37), examining the thermal stability properties of polysiloxanes with different arrangements of methyl and phenyl groups in the chain, concluded that the overall ratio of Me:Ph was the only important factor.

The inclusion of p-silphenylene units in the backbone of polysiloxanes has been shown to improve greatly the thermal stability of these polymers (Refs: 38, 39). The greater rigidity of the chains and the greater strength of the Si-C bond are thought to be the reasons for the increased stability.

1.5 Aim of this Work

The aim of this work is to prepare and characterise pure samples of high molecular weight polysiloxanes with varying arrangements of methyl and phenyl side groups, and to study their thermal decomposition under vacuum. The work has concentrated on such features as detailed analysis of products, the effect of the molecular weight of the polymers, changes in the involatile residue, the arrangement of methyl and phenyl side groups and the effect of blocking chain ends.

CHAPTER 2

EXPERIMENTAL TECHNIQUES

2.1 Sources of Reagents

Dichlorodimethylsilane was obtained from two sources:

a) Peninsular Chemical Research Inc., Florida, U.S.A. (repackaged as Dow Corning Z-129 Silane).

b) E. Merck Laboratories (Germany). Specification 99% (GLC), D_4^{20} 1.074 - 1.076, trichloromethylsilane 0.2%, monochloromethylsilane 0.1%.

Dichlorophenylsilane was obtained from Fluka (Switzerland) and labelled pure.

Dichloromethylphenylsilane was obtained from two sources:

a) Aldrich Chemical Co. Inc. (U.S.A.) Purity checked by IR.

b) Midland Silicones, repackaged by Hopkin & Williams Chemicals Ltd.

1,1,1,3,3,3, Hexamethyldisilazane was obtained from Merck Chem. Co. (Germany).

Hexamethylcyclotrisiloxane was obtained from P.C.R. Laboratories (U.S.A.) Cat. No. 2866

Decamethylcyclopentasiloxane was obtained from I.C.N. K & K Laboratories (U.S.A.) Cat No. 2866

Tetramethylammoniumhydroxide was obtained as a 25% aqueous solution from Hopkin & Williams Ltd.

Di-(4-isocyanatophenyl)-methane was obtained from B.D.H. Chemicals Ltd.

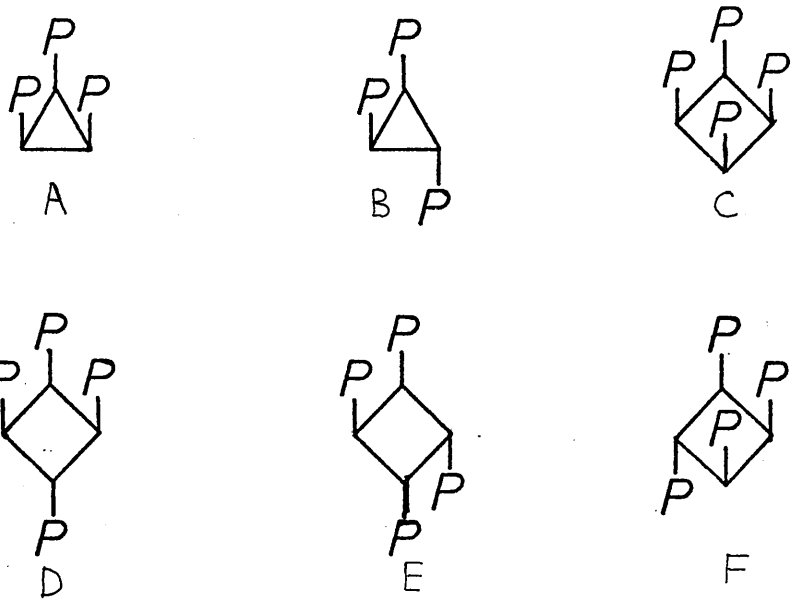
All other reagents and solvents used in this study were AnalaR grade.

2.2 Preparation of Polymers

Introduction

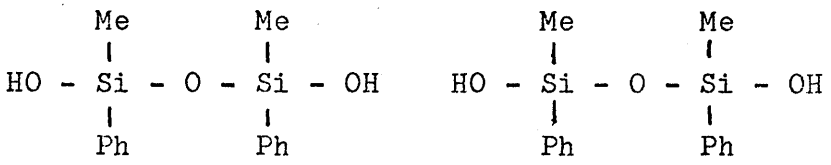
(i) Linear polysiloxanes were prepared by the rearrangement of cyclic trimer or tetramer siloxanes catalysed by tetramethylammoniumhydroxide. The individual cyclic siloxanes were prepared by hydrolysis of the corresponding dichlorosilanes.

Hickton et al (Ref:40) give details of the preparation and isolation of the following methyl/phenyl cyclic trimer and tetramer isomers.



The authors of this paper also suggest a method of preparing cyclic siloxanes by the reaction of an $\alpha-\omega$ siloxane diol with a dichlorosilane ("diol ring closure" reaction). The diols they used were the meso

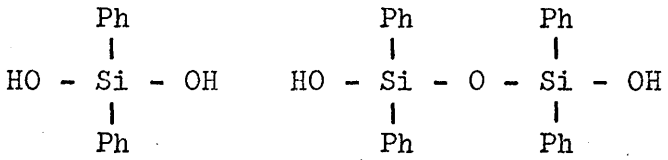
and racemic isomers of 1,3, dimethyl, 1,3, diphenyl/ disiloxane diol as prepared by Daudt and Hyde (Ref:41)

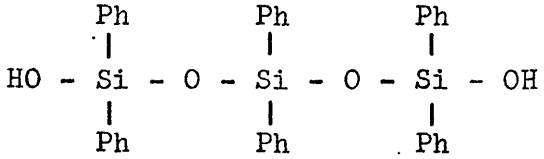


Meso (M.Pt. 110°C) Racemic (M.Pt. 100°C)

Patnode and Wilcock (Ref:16) have found the major products of hydrolysis of dimethyldichlorosilane - with no pH control of the reaction mixture - to be mainly cyclic trimer, tetramer and pentamer compounds.

Harris (Ref: 42), however, has shown that short chain α-ω diols can be isolated from the hydrolysis of dimethyldichlorosilane when the temperature and pH of the reaction are closely controlled. Harris has also prepared the following α-ω diphenylsiloxane diols,

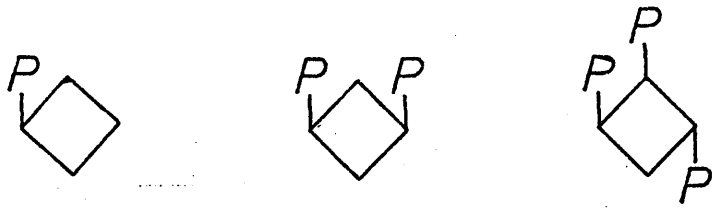




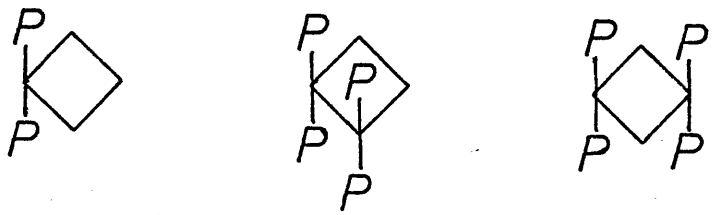
using a similar method.

Various workers have reported the cohydrolysis of mixtures of different dichlorosilanes.

Andrianov and Yakushkina (Ref: 43) have cohydro/ lysed dimethyldichlorosilane and methylphenyldichloro/ silane and have isolated the following mixed isomers:



Andrianov et al (Ref: 44) describe the cohydrolysis of dimethyldichlorosilane and diphenyldichlorosilane and the subsequent isolation of the following cyclics:



(ii) Hydrolysis of Dichloromethylphenylsilane

a) Preparation of 1,3, dimethyl, 1,3, diphenyldisiloxane diols

40g of dichlorophenylmethylsilane in 200ml of ether was added dropwise, with stirring, to 500ml of a 10% ammonium hydroxide solution cooled in an ice/water mixture. The ether layer was separated and washed with sodium bicarbon/ ate solution (twice) and distilled water until neutral.

Evaporation of the solvent gave a greasy solid (33g) which was fractionally recrystallised from light petroleum ether to give the meso and racemic isomers of 1,3, dimethyl, 1,3, diphenyldisiloxane diol (7.8g and 3.2g respectively).

The melting points (110°C for the meso and 100°C for

the racemic isomer) agreed with those obtained by Hickton et al (Ref: 40) and the compounds are further characterised by IR and NMR.

b) Preparation of cyclics

500g of dichlorophenylmethylsilane in 1500ml of ether was added dropwise, with stirring, to an excess of water at $0^{o}C$.

The ether layer was separated and washed with sodium bicarbonate solution (twice) and with distilled water until neutral. Evaporation of the solvent gave a clear oil (290g) consisting mostly of cyclic trimer and tetramer.

Distillation of this oil under vacuum gave four fractions collected between 140^{o} and $190^{o}C/0.1mmHg$. The first two fractions consisted predominately of cyclic trimers and the later two were mainly cyclic tetramers. Separation of the isomers was partly effected by adding an equal volume of light petroleum ether to the fractions and storing them at $-25^{o}C$. Within 24 hours isomer A began crystallising from the trimer fractions followed by isomer B after about one week. Small amounts of isomers A and B were collected from the tetramer fractions after about four weeks, followed by isomer C. Attempts to isolate isomers D, E and F were unsuccessful.

The isomers were identified by mass spec., NMR and by their melting points (Ref: 21).

(iii) Hydrolysis of Dichlorodimethylsilane

a) Preparation of dimethylsilane diol

130g of dichlorodimethylsilane was added dropwise, over $2\frac{1}{2}$ hours to a stirred mixture of 165g of ammonium carbonate in 820ml of water at $0^{o}C$. The mixture was then saturated with sodium chloride and extracted repeatedly with ether. The solvent was removed from the combined ether extractions giving a greasy solid which was washed with light petroleum ether and recrystallised from n-pentane/ ether giving 38g of pure dimethylsilane diol (melting point $100.5^{o}C$).

The diol was characterised by IR and NMR.

b) Preparation of 1,1,3,3, tetramethyldisiloxane diol

130g of dichlorodimethylsilane was added to 220g of ammonium carbonate in 820ml of water (conditions as above). The solution was saturated with sodium chloride and stored at $-5^{o}C$ for 2 days. The crystals so formed were collected and recrystallised from light petroleum ether giving 32.3g of 1,1,3,3, tetramethyldisiloxane diol (melting point $68.5^{o}C$) characterised by IR and NMR.

(iv) Hydrolysis of Dichlorodiphenylsilane

100g of dichlorodiphenylsilane in 100ml of ether was added, with stirring to a large excess of water at $0^{o}C$. The solid material formed was filtered, washed with distilled water and dried. It was then recrystallised from methyl acetate giving white needle crystals melting at $148^{o}C$, and characterised by IR and NMR.

b) Preparation of I,I,3,3, tetraphenyldisiloxane diol and I,I,3,3,5,5, hexaphenyltrisiloxane diol.

380g of dichlorodiphenylsilane was added dropwise, over 45 minutes, to a stirred mixture of 330g of ammonium carbonate, I400ml of ether and 27ml of water at room temperature. The mixture was refluxed for I2 hours and then 500ml of water were added. The ether layer was separated and washed with sodium bicarbonate solution (twice) and distilled water until neutral. The solvent was removed and the remaining solid was extracted many times with toluene which was then evaporated off leaving a white solid which was fractionally recrystallised from toluene/light petroleum ether to give I,I,3,3, tetraphenyldisiloxane diol (yield I50g, melting point II5^{o}C) and I,I,3,3,5,5, hexaphenyltrisiloxane diol (yield 50g, melting point II2^{o}C).

The diols were characterised by IR and NMR.

(v) Preparation of Mixed Cyclics

a) Cohydrolysis of dichlorodimethylsilane and dichloromethylphenylsilane.

A. 75g of dichlorodimethylsilane and 25g of dichloro/methylphenylsilane were added dropwise, with stirring, to I00ml of water and I00ml of ether at room temperature. The ether layer was separated and washed until neutral and the solvent evaporated, leaving an oil. This was fractionally distilled giving octamethylcyclotetrasiloxane (boiling point I74-I76^{o}C (I3g)) and heptamethylphenylcyclotetra/siloxane (boiling point 88^{o}C/3.0mmHg(28g)). The latter was characterised by mass spec., IR and NMR.

B. 382g of dichloromethylphenylsilane and 80g of dichloro/dimethylsilane were treated as above. The resultant oil (after removal of the solvent) was vacuum distilled and the fraction boiling at I78-I79°C/0.6mm$_{Hg}$ was found to be a mixture of the three $D_1D'_3$ isomers (characterised by NMR and mass spec.).

b) Cohydrolysis of dichlorodimethylsilane and dichlorodiphenylsilane.

I30g of dichlorodimethylsilane and I25g of dichloro/diphenylsilane was added dropwise, to a stirred mixture of I00ml of water and I50ml of ether at room temperature.

The ether layer was separated, washed until neutral and the solvent was then removed. The resulting oil was vacuum distilled and 5 fractions, boiling point I20-I80°C/0.6mm were collected. NMR analysis showed fractions I, 2 and 3 contained mainly $D_2D''_1$, $D_3D''_1$ and $D_4D''_1$ whereas fractions 4 and 5 contained mainly $D_2D''_2$. Fractions 4 and 5 were mixed with an equal volume of light petroleum ether and stored at -25°C.

After about 5 days crystals of $D_2D''_2$ (I,I',5,5' isomer) were collected followed about I0 days later by crystals of the I,I',3,3' isomer. These were recrystallised from methanol and characterised by melting point (I39°C and 75°C respectively) mass spec. and NMR.

Successive vacuum distillations of fractions I, 2 and 3 were carried out to separate pure $D_3D''_1$ (boiling point I22°C/0.3mmHg) which was characterised by mass spec. and NMR.

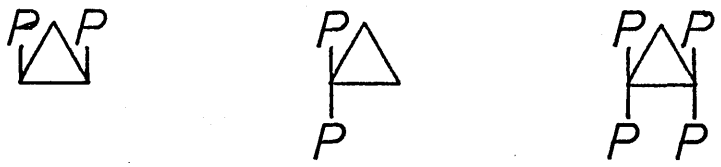
c) 'Diol ring closure' preparations.

These preparations involved reaction of the previously prepared siloxane diols with a dichlorosilane to form a mixed cyclic.

Typically 9g of I,I',3,3', tetramethyldisiloxane diol and 36ml of triethylamine in 250ml of anhydrous ether were cooled in an ice-bath and I5g of dichloromethylphenylsilane in I00ml of anhydrous ether were added dropwise, with stirring, over 3 hours.

The ether solution was then washed and the solvent removed. The resulting oil was vacuum distilled (boiling point 68°C/I.5mmHg) to give pure $D_2D'_1$.

This method was also used to prepare the following mixed cyclics:

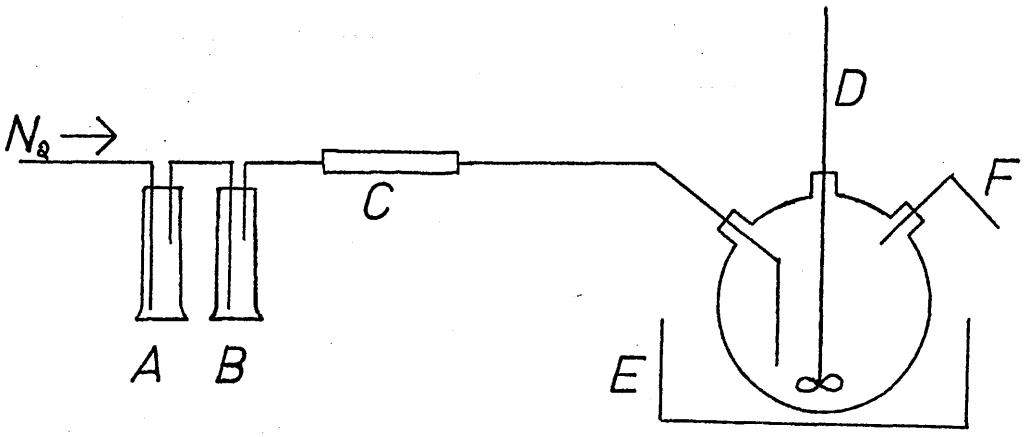


(vi) Polymerisation of Cyclic Siloxanes

The polymerisations were carried out in bulk, under a stream of nitrogen (British Oxygen Co. 'White Spot') using tetramethyl ammonium hydroxide as catalyst. A schematic description of the polymerisation apparatus is shown in Figure 2:I.

Typically the cyclic siloxane (2-5g) was weighed into a three necked R.B. flask, fitted with a mechanical stirrer and an inlet for nitrogen. The flask was placed in a thermostatically controlled oil bath, heated to the

Figure 2.1 Polysiloxane Polymerisation Apparatus



A - Solution of Pyrogallol

B - Drying Bottle - (Silica Gel)

C - Drying Tube (Silica Gel)

D - Mechanical Stirrer

E - Thermostatically Controlled Bath

F - Nitrogen Outlet

required temperature (110°C-120°C) and flushed with nitrogen to remove oxygen. The catalyst (0.01-0.1 wt.%) was added via the third inlet and the reaction was continued until no further increase in the viscosity of the polymer was observed. The flask was heated to 140°C for 15 minutes to destroy the catalyst, and then allowed to cool. The polymer was dissolved in toluene and reprecipitated from methanol (twice) to remove residual low molecular weight cyclics and the products of decomposition of the catalyst (methanol and trimethylamine). The polymer was finally dried at 50°C (48 hours) in a vacuum oven.

In every case the polymers obtained were clear gums or viscous liquids, depending upon their molecular weight and phenyl content.

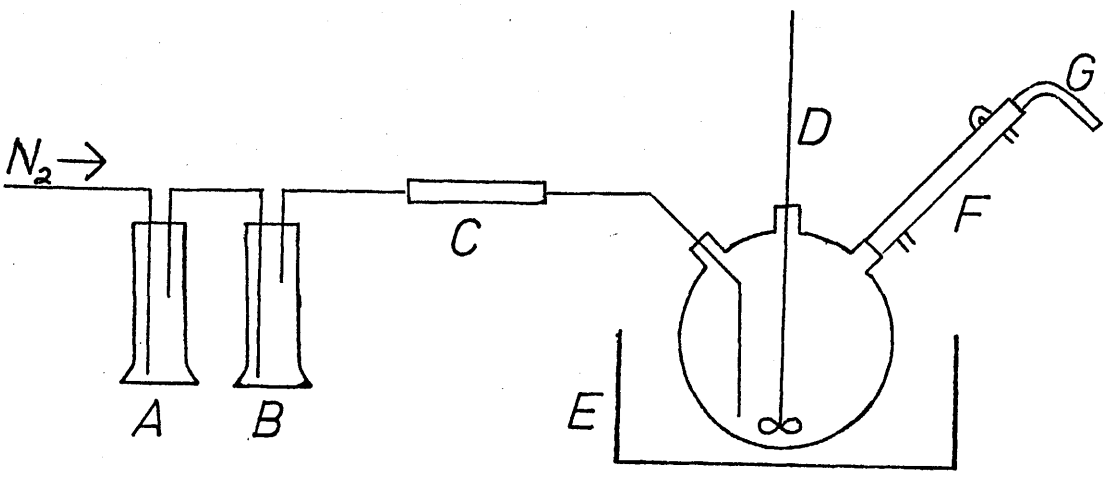
The polymers were characterised by IR, NMR and molecular weight (number average).

(vii) End Blocking of Polysiloxanes

Conversion of the hydroxyl end groups of linear poly/siloxanes to their trimethylsiloxy analogues was carried out as follows:

The polymer (1.0g) was dissolved in 1,1,1,3,3,3, hexamethyldisilazane (20ml) and refluxed for 48 hours. It was then reprecipitated from methanol (twice) and dried in a vacuum oven for 48 hours (at 50°C). This procedure did not affect the molecular weight of the starting polymer.

Figure 2.2 Siloxane - Urethane Copolymerisation Apparatus



A - Solution of Pyrogallol

B - Drying Bottle

C - Drying Tube

D - Mechanical Stirrer

E - Thermostatically Controlled Bath

F - Water Cooled Condenser

G - Drying Tube

(viii) Preparation of Siloxane-Urethane Copolymers

These polymerisations were carried out in solution (toluene) under a stream of nitrogen with the apparatus described in Figure 2:2.

Typically, 0.0I2 moles of siloxane diol were weighed into a three necked R.B. flask (fitted with a nitrogen inlet and a mechanical stirrer) containing 0.0I0 moles of M.D.I. in 50ml of toluene. The flask was then flushed with nitrogen and heated under reflux for about 3 hours. The white precipitate which formed was filtered, washed with toluene (to remove any unreacted monomers) and ether. The copolymers were finally dried in a vacuum oven at 40°C (48 hours) and characterised by IR (KBr disc.).

2.3 Thermal Methods of Analysis

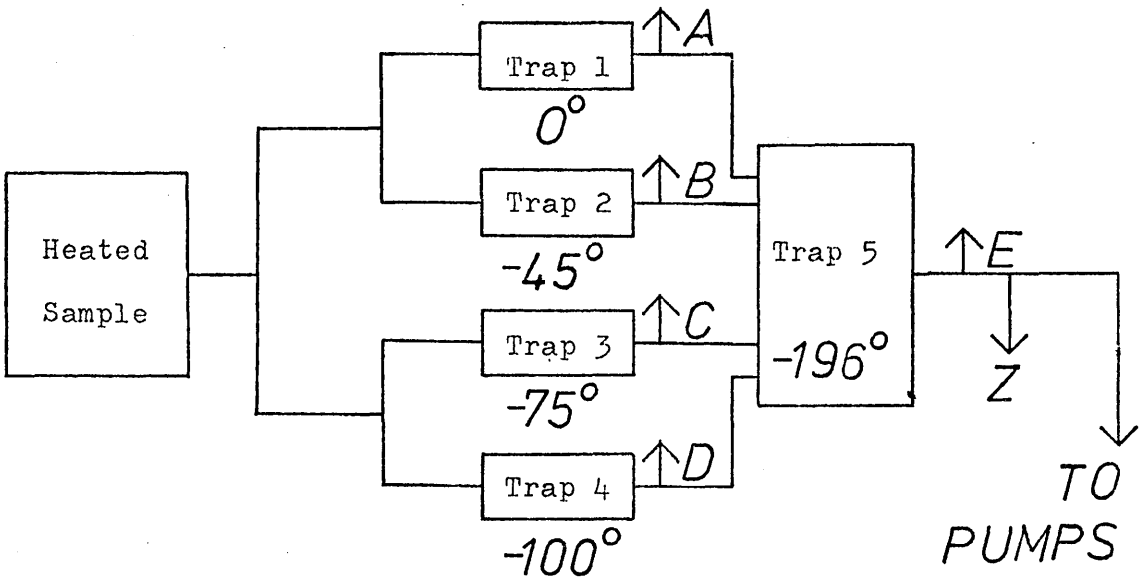
(i) Thermogravimetric Analyses (T.G.A.)

Thermogravimetric analyses were carried out on the Dupont 950 instrument. The samples (I0mg) were placed in a platinum holder and heated at I0°C/min. from ambient to 800°C in a dynamic atmosphere of oxygen-free nitrogen (80ml/min.).

(ii) Thermal Volatilisation Analyses (T.V.A.)

T.V.A. has been used to study the degradation properties of many polymers and is now a well established technique (Ref:45).

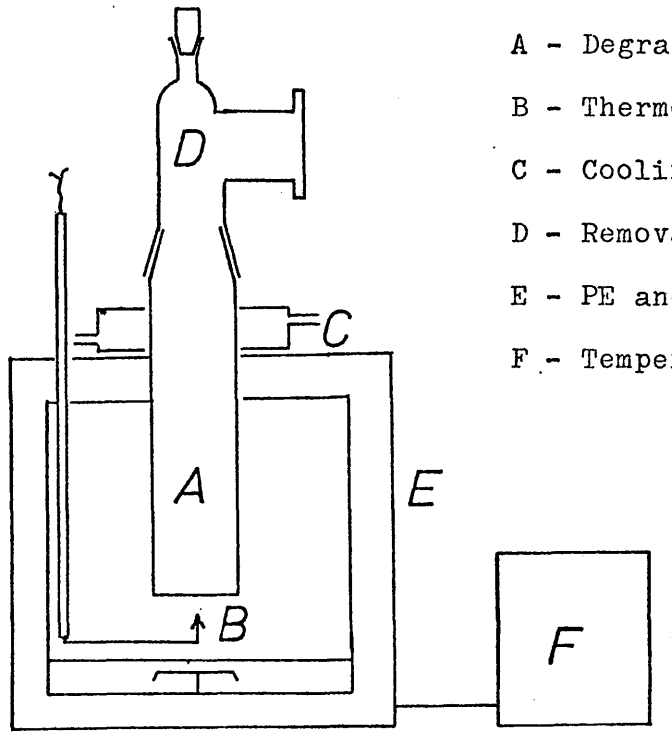
Figure 2:3 shows a schematic diagram of the experimental layout.



A,B,C,D and E are Pirani Guage Heads

Z is Sample Receiving Tube or Gas Cell

Figure 2.3 (a) Thermal Volatilisation Analyser



A - Degradation Tube

B - Thermocouple

C - Cooling Jacket

D - Removable Socket Joint

E - PE and Fll Oven

F - Temperature Programmer

Figure 2.3 (b) TVA Heating Assembly

The sample is heated on the base of a 6" long glass tube, made from a Pyrex FG 35 flange. The tube is heated in a Perkin Elmer FII oven, equipped with a linear temperature programmer, at 10°C/min. from ambient to 500°C - the temperature being measured by a chromel - alumel thermocouple fixed near the base of the tube. During the experiment, the top of the tube and the greased flange joint are cooled by a water jacket.

The volatile products of degradation pass along four routes (geometrically equivalent) each containing a trap at a different temperature (0°C, -45°C, -75°C and -100°C, respectively). The four routes then pass through a common trap at -196°C. Pirani gauges are placed after each trap and their outputs, as well as the oven temperature, are fed, via a multihead switch unit, into a 12 channel recorder. It can be shown empirically that the same quantity of volatiles passes into each of the four routes, but when a trap is reached, one or more of the components may be condensed out so that the Pirani output traces are often non-coincident. By means of spectroscopic analysis of the products and by the known behaviour of various substances in the four traps, it is often possible to obtain a useful qualitative picture of the degradative properties of a polymer.

Product analysis of T.V.A. fractions

The volatiles fall into two categories:

a) condensables, b) non-condensables.

The 'condensables' are those volatiles which condense in a continously pumped system at -196°C and thus are easily

analysed by distillation into an appropriate collecting device (e.g. IR gas cell).

'Non-condensables' do not condense at -196°C and can thus only be collected from 'closed system' degradations.

The 'cold-ring fraction' is made up of products volatile only at oven temperatures. These products, therefore, condense on the upper parts of the degradation tube where they can be removed for subsequent analysis.

The involatile 'residue' may be analysed as a solution (if not cross-linked) or as a solid.

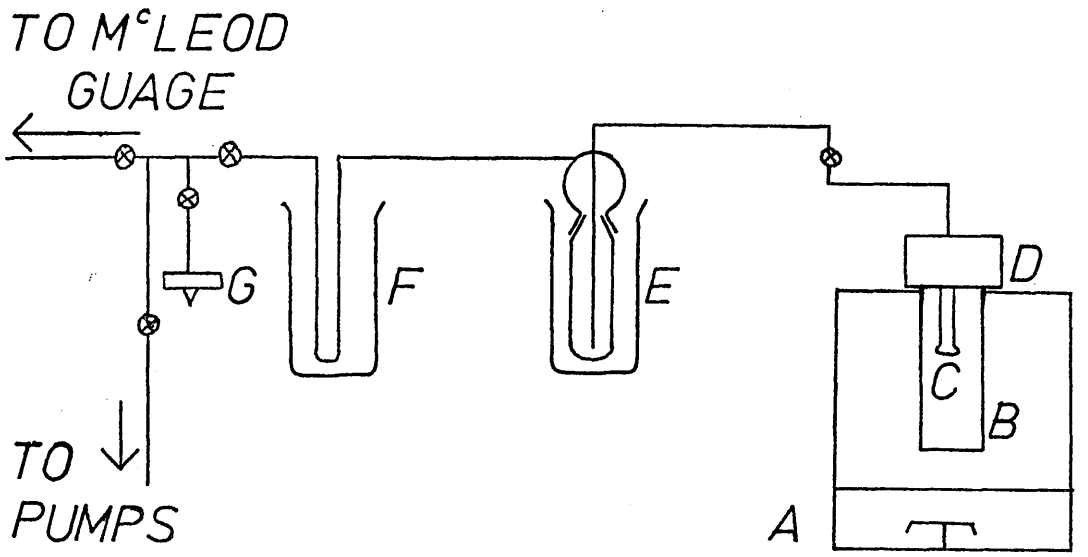
(iii) Vacuum Line Degradation System

This system which is illustrated in Figure 2.4, was used to study the degradation properties of polysiloxanes in a continously pumped high vacuum system.

The sample (100mg) was weighed into a small aluminium boat which was then placed in the degradation tube. The evacuated tube (10^{-6} torr) was heated by a Perkin Elmer FII oven to the required temperature which was measured by a chromel-alumel thermocouple placed near the base of the tube.

The main degradation products, cyclic siloxanes, collect on the cold finger except for hexamethyltrimer and octa/methyltetramer cyclics, which condensed out in the first trap (at -70°C). All other condensables (in practice only benzene) are collected in the second trap (at -196°C). The siloxane cyclics are easily collected by washing the cold finger and the first trap with a suitable solvent (carbon tetrachloride, ether etc.) for further analysis by NMR, GLC

Figure 2.4 Vacuum Line Degradation System



A - P.E. F11 Oven

B - Degradation Tube

C - Cold Finger

D - Water Cooled Jacket

E - -70°C Trap

F - -196°C Trap

G - Gas Cell

or GCMS.

2.4 Analytical Techniques

(i) Infra-Red Spectroscopy

Spectra were recorded on a Perkin Elmer 257 grating spectrometer. Polysiloxane polymers and cold-ring fractions were run in solution; siloxane-urethane copolymers, cold-ring fractions and residues as KBr discs; and volatile products were examined in the gaseous phase.

(ii) Mass Spectrometry

The mass spectra of various reference siloxane ring compounds and non-condensable degradation products were obtained using an AEI MSI2 mass spectrometer operating at 70ev.

(iii) Gas-Liquid Chromatography (GLC)

GLC analyses were carried out using the Micro Tek G.C. 2000 -R instrument which has a flame ionisation detector and linear temperature programmer.

Quantitative analysis were carried out with the aid of an Infotronics 309 Digital Microprocessor (for the measurement of peak areas) after calibration of the flame ionisation detector (see below).

Three columns were used for the separation of the cyclic siloxane degradation products:
I% OV1 (IO'), 2.5% OV1 (5'), and 3% Dexsil (6').

Quantitative estimation of cyclic siloxanes

Data for the quantitative examination of cyclic siloxanes, were obtained using the 'Normalisation Method' described by Grant (Ref:46).

The flame ionisation detector was first calibrated with pure compounds to obtain their relative response factors (Rf).

The Rf value is calculated from the peak areas of calibration mixtures and from the weights of the compounds in the mixture. In this method, the selected standard need not be a specially added compound but can be any compound known to be present in the mixture. Thus the relative response factors are calculated from the following relationship:

$$Rf = \frac{Ai \times Ws}{As \times Wi}$$

where Rf is the relative response factor

As is the area of standard

Ai is the area of component

Ws is the weight of standard

Wi is the weight of component

The Rf value is therefore the gradient of a plot of (Ai/As) vs (Wi/Ws).

The concentration (% wt) of each component in the mixture is given by:

$$Ci = \frac{Ai/Rfi}{\sum(A/Rf)} \times 100$$

A set of Rf values was calculated for possible degradation products from each of the three polysiloxane polymer series, using the cyclics which could be synthesised.

Rf values for those cyclics which could not be isolated were estimated. Tables 2.1, 2.2 and 2.3 show the Rf values for each of the three polysiloxane series. Figure 2.5 shows a typical graph for determining an Rf value, namely D_4' vs D_3' .

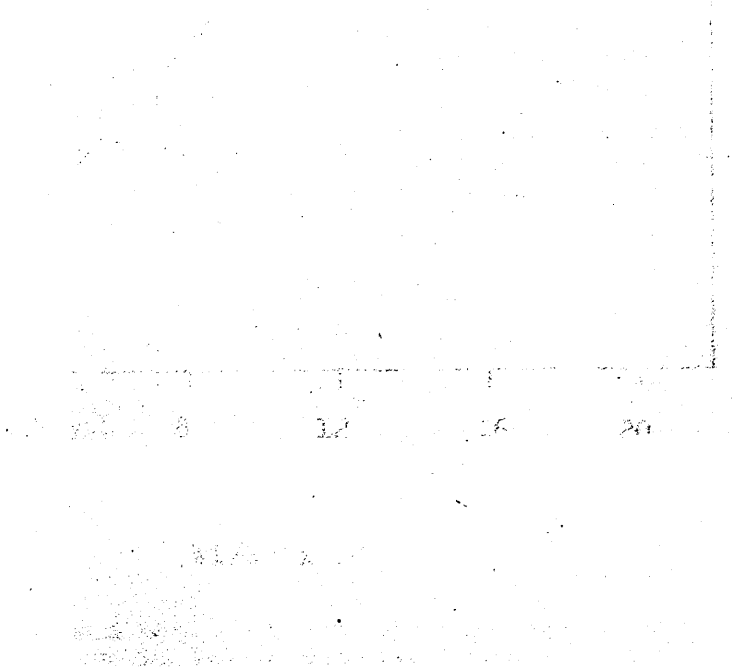
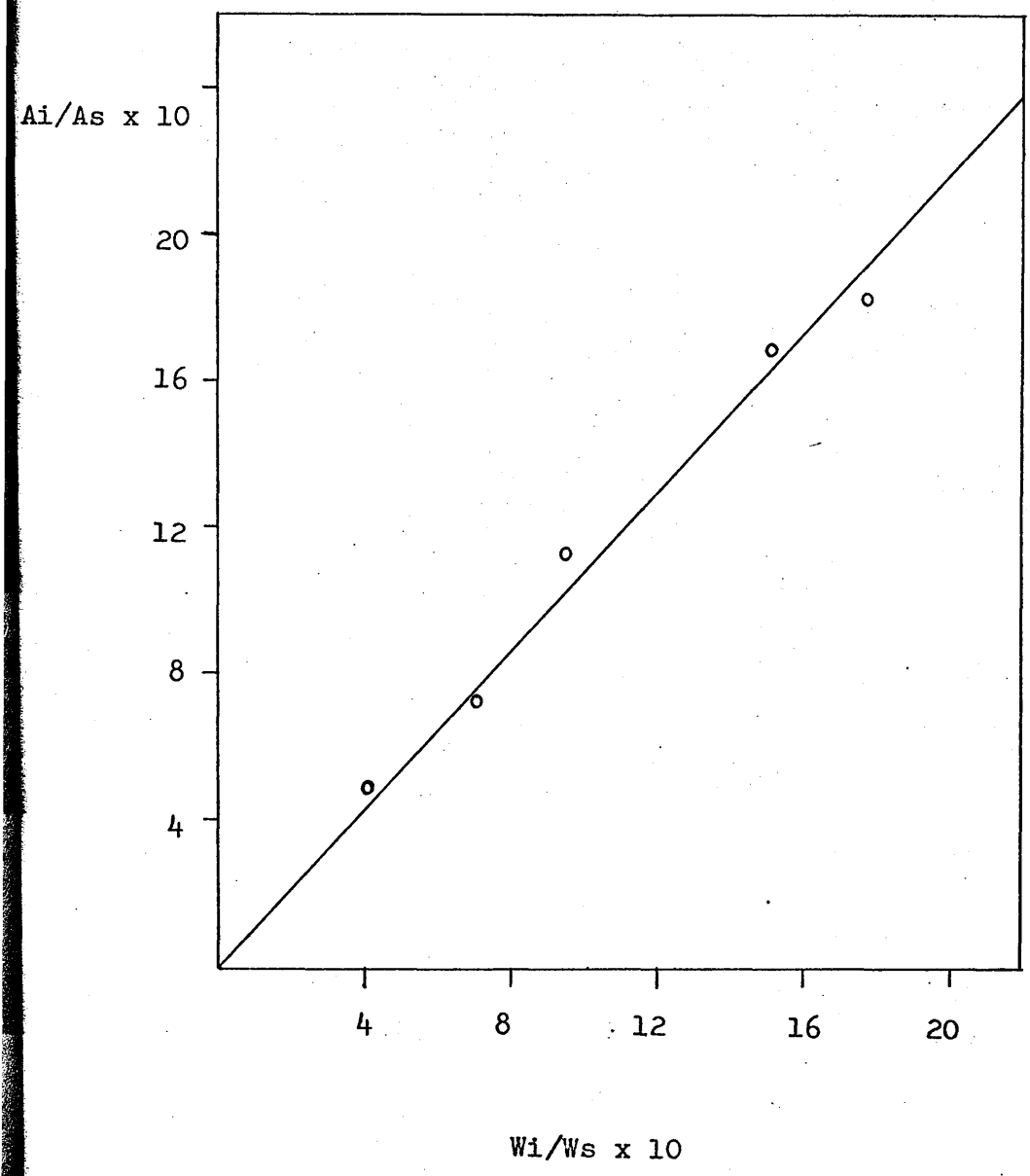


Figure 2.5 Plot of Ai/As vs Wi/Ws for $D_{3(s)}'$ vs $D_{4(i)}'$ —



$\therefore$ Rf = gradient

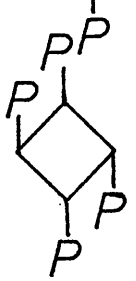
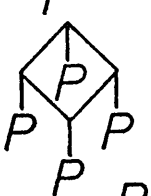
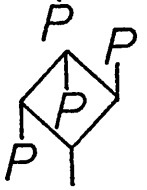
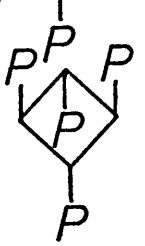
$= \frac{21.6}{20}$

$= 1.08$

TABLE 2.I

GLC Detector Response Data

(Relative to trans D_3^1)

Oligomer	Rf
	I.00
	I.00
	I.08
	I.08 *
	I.08 *
	I.08 *
D_5 isomers	I.II *

* estimated value

TABLE 2.2

GLC Detector Response Data

(Relative to D_2D_1')

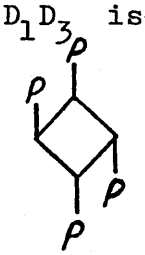
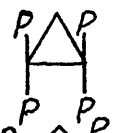
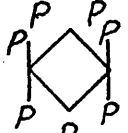
Oligomer	Rf
	0.88
	0.92
	0.94
	I.00
	I.02
	I.04
	I.07
D_1D_3 isomers	I.09
	I.II

TABLE 2.3

GLC Detector Response Data

(Relative to D_2D_1'')

Oligomer	Rf
	0.86
	0.89
	0.9I
	I.00
	I.02
	I.II
	I.I5
	I.I5
	I.20

(iv) Gas Chromatography - Mass Spectrometry GCMS

LK 9000 (LKB Produkter) and AEI 30 instruments were used to identify polysiloxane degradation products. The spectrometers are single focusing instruments with a fast scanning speed. As the individual components are detected on leaving the GLC column, pressing the scan button increases the ionisation voltage to 70 e.v. and a mass spectrum is obtained on the UV recorder.

(v) Ultra-Violet Spectroscopy (UV)

A unicam SP800 spectrometer was used to study the evolution of benzene as a degradation product from the polysiloxanes - all samples being run in the gaseous phase.

Quantitative estimation of benzene

The absorbance at 254nm of known pressure of benzene was measured on the SP800 instrument and a calibration graph (Figure 2.6) was constructed (absorbance vs pressure).

The pressure in the gas cell at low pressures (0.02 cm Hg) was measured by a McLeod Gauge and by a mercury manometer at higher pressures.

Knowing the volume of the gas cell, the amount of benzene (in moles) can be calculated from the gas equation:

$$PV = nRT \quad \text{(assuming ideal behaviour)}$$

where/

Figure 2.6 (a)

Calibration Curve

Pressure of Benzene vs Absorbance

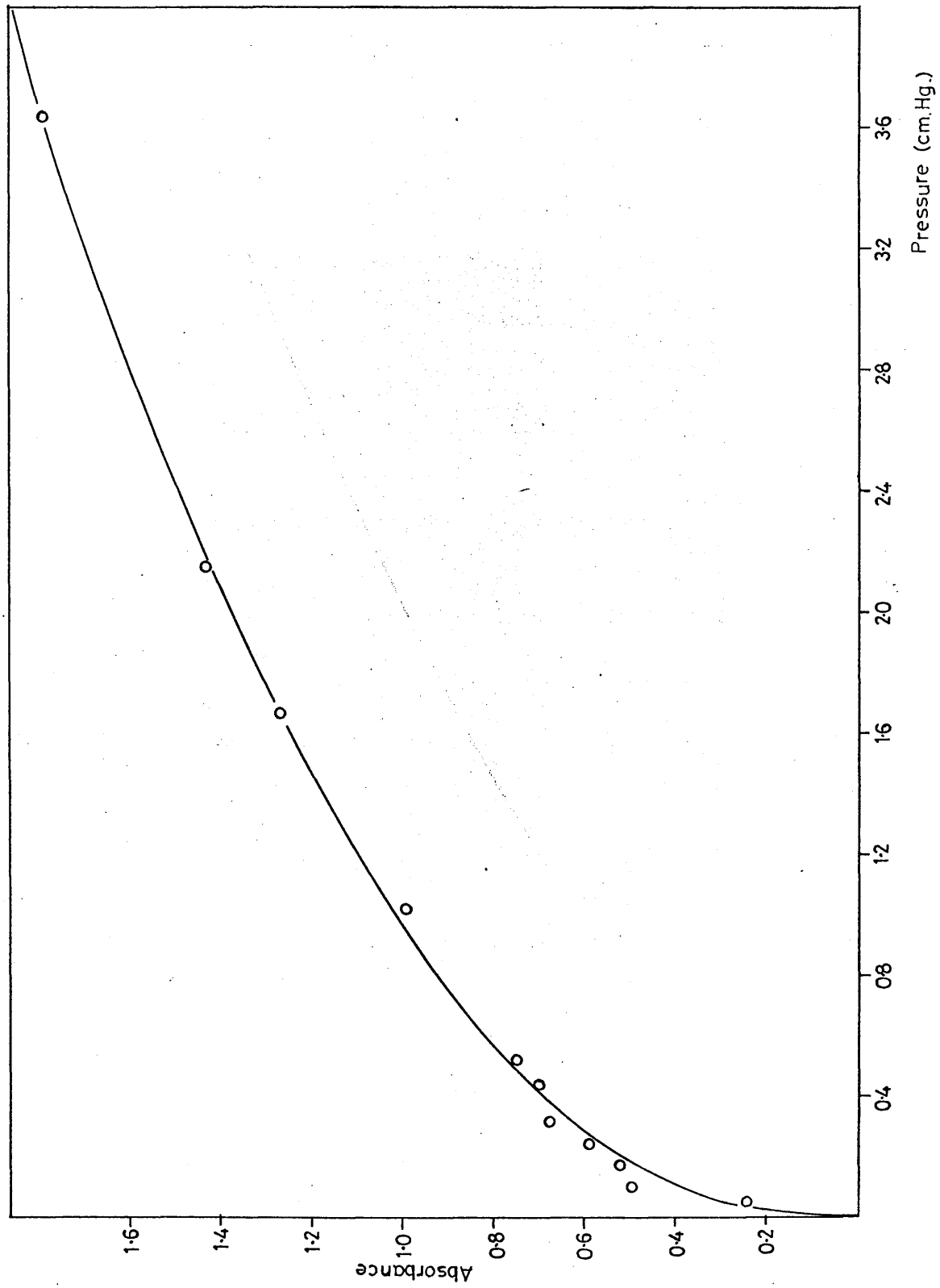
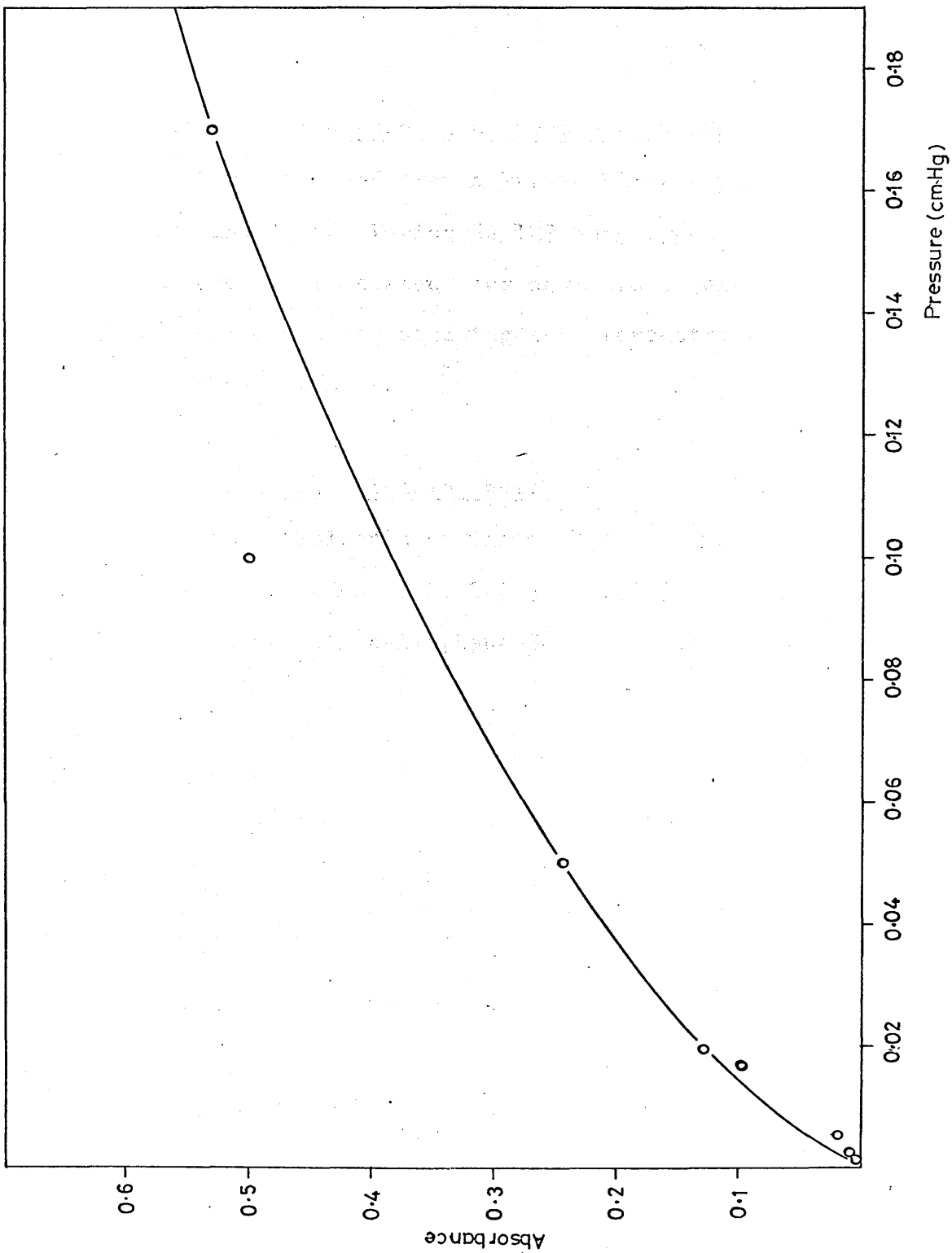


Figure 2.6 (b)

Calibration Curve



where P = Pressure of benzene (cm Hg)

V = Volume of gas cell (ml)

n = No. of moles of benzene

R = gas constant (ml cm Hg mol $^{-1}K^{-1}$)

T = temperature (K)

(vi) Nuclear Magnetic Resonance Spectroscopy NMR

Spectra were obtained from a Perkin Elmer RIO 60 MHz spectrometer and from a Varian HA IOO MHz spectrometer.

NMR was used in this study for analysis of siloxane diols and cyclics and for studying the micro-structure of the polysiloxane polymers.

(vii) Measurement of Molecular Weight

Number average molecular weights of the polysiloxane polymers were measured on a Hewlett-Packard 50I High Speed Membrane Osmometer with cellophane 300 membrane.

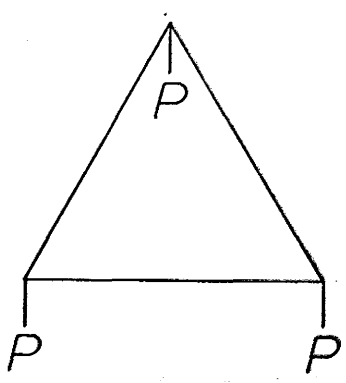
CHAPTER 3

Poly(Methylphenylsiloxane)

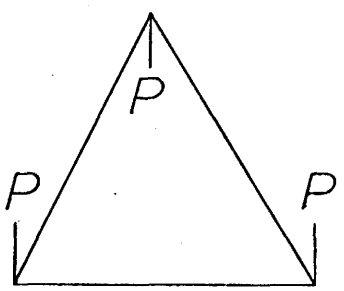
3.1 Introduction

Work to be described in this chapter relates to the preparation and thermal degradation of polysiloxanes with a methyl and phenyl group on each silicon atom, i.e. polymethylphenylsiloxane (PMPS).

Although Kipping and other workers had previously prepared organo silicon compounds with methyl and phenyl groups, Lewis (Ref: 47) was the first to describe the hydrolysis of dichloromethylphenylsilane and subsequent isolation of two D_3' isomers for which he proposed the following structures:



cis M.Pt. 99.5°C



trans M.Pt. 39.5°C

He also proposed that the methylphenyl tetramer would show similar isomerism but was unable to separate any of the four possible structures.

All attempts (Refs: 48,49) to isolate successfully the four tetramer isomers failed until Hickton et al (Ref: 40) succeeded in 1966, using preparative GLC. They also showed that proton NMR was potentially a very valuable tool for identifying methyl and phenyl containing cyclic siloxanes, as the methyl proton shifts for these compounds depended only on the size of the ring and the positions of neighbouring phenyl groups. This idea was later followed up by Williams et al (Ref:50) who produced an equation which could predict the methyl proton shifts in any trimer, tetramer and pentamer siloxanes with methyl and/or phenyl groups.

In 1966, Andrianov et al (Refs: 51, 52) failed to produce high molecular weight polymers from methylphenyl tetramer although they were able (Ref: 52) to polymerise both trimer isomers. They found that the cis isomer polymerised more readily than the trans isomer, which was due, they claimed to the increased steric strain in the former. Andrianov et al (Ref:53), in a study of the polymerisation kinetics of cis D_3' in benzene, found the reaction to be first order with respect to monomer and catalyst and that depolymerisation also took place with the formation of some tetramer.

Andrianov (Ref: 54) has shown that stereo-regular polymers can be prepared if the configuration of the monomer is not lost on ring opening during polymerisation.

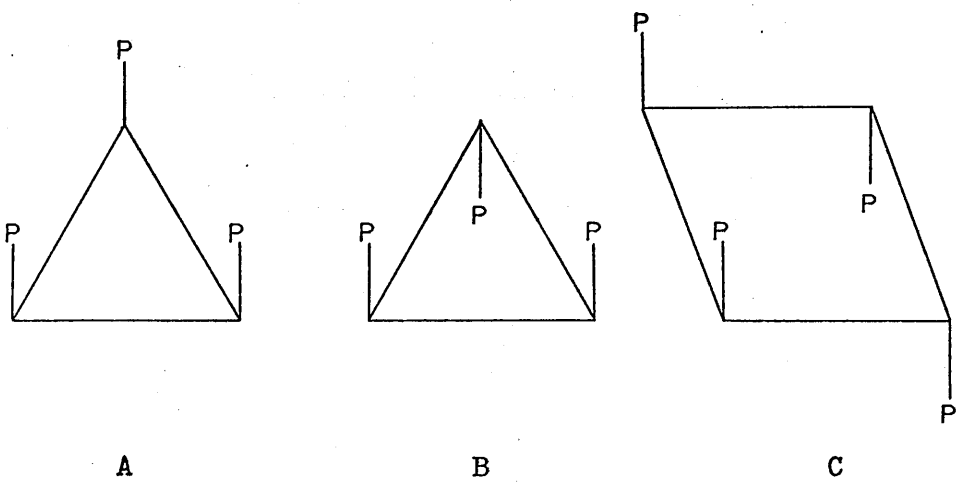
He demonstrated, using proton NMR, that cis D_3' can form a stereoregular polymer, but that a mixture of cis and trans D_3' cannot. Again, some D_4' was formed during the reaction.

Although industry has long used phenyl containing polysiloxanes, the thermal degradation of PMPS has been little studied. Sobolevskii et al (Ref: 55) have demonstrated that PMPS end-blocked with trimethylsilyl groups is less stable, thermo-oxidatively than PMPS end-blocked by triphenylsilyl groups.

In 1970, Thomas and Kendrick (Ref: 21) reported the degradation products of PMPS, end-blocked with trimethyl/silyl groups, to be trans D_3' and D_4' isomers with no evidence of Si-C bond rupture at 400°C, although other workers (Refs: 27, 56) investigating cross-linked PMPS, have found hydrogen, methane and benzene as degradation products. Sobolevskii et al (Ref: 28) have also found hydrogen and benzene as degradation products from oligomethylphenyl siloxanes.

3.2 Preparation of Methyl Phenyl Cyclics

Methylphenyl cyclic siloxanes were prepared as described in Chapter 2. Of the six possible trimer and tetramer isomers only the following were isolated in pure form:



A B C

These were characterised as shown in Table 3.1 and their purity ($>$99.9%) was checked by GLC.

3.3 Preparation of Polymethylphenylsiloxane

A total of seven polymers (two of which were end-blocked) have been prepared using the polymerisation conditions shown in Table 3.2.

Attempts to produce stereoregular polymers by the polymerisation of the different isomers were unsuccessful- all polymers prepared were found to be atactic by NMR analysis (Figure 3.1)(Ref: 54).

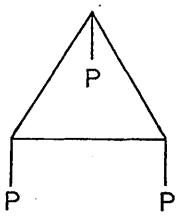
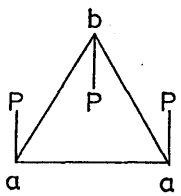
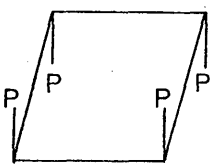
3.4 T.G.A.

The analyses were carried out as described in Chapter 2.

TGA traces for polymers A, B, D and E are shown in Figure 3.2. Figure 3.3 shows a plot of % weight of the

TABLE 3.1

Characterisation of Methyl Phenyl Cyclics

Isomer Structure	Mass spec (Parent ion)	IR± (Characteristic bands cm^{-1})	NMR* (Methyl Protons τ)	M.Pt* (^{o}C)
	408	i) 1000-1100 ii) 1260 iii) 1430	9.484	99.5
	408	i) 1000-1100 ii) 1260 iii) 1430	a)9.557 b)9.622	44-46
	529	i) 1000-1100 ii) 1260 iii) 1430	9.719	99-100

*The values for NMR shifts and M.Pts concur with those given by Hickton et al (Ref: 40)

±The IR bands (Ref: 57) are characteristic of

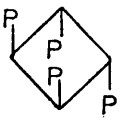
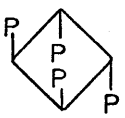
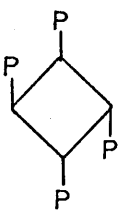
(i) Si-O-Si stretch

(ii) $Si-CH_3$ symmetric deformation

(iii) Si-Phenyl stretch

TABLE 3.2

Preparation of Polymethylphenylsiloxanes

Polymer	Monomer	Polymerisation Temperature (°C)	Catalyst Concentration (w/w%)	$\bar{M}n$
A		120	0.02	211000
B		120	0.02	200000
C	End-blocked sample of Polymer B			200000
D		120	0.01	121000
E	Mixture of Cyclics	115	0.01	55700
F	Mixture of Cyclics	120	0.02	30000
G	End-blocked sample of Polymer F			30000

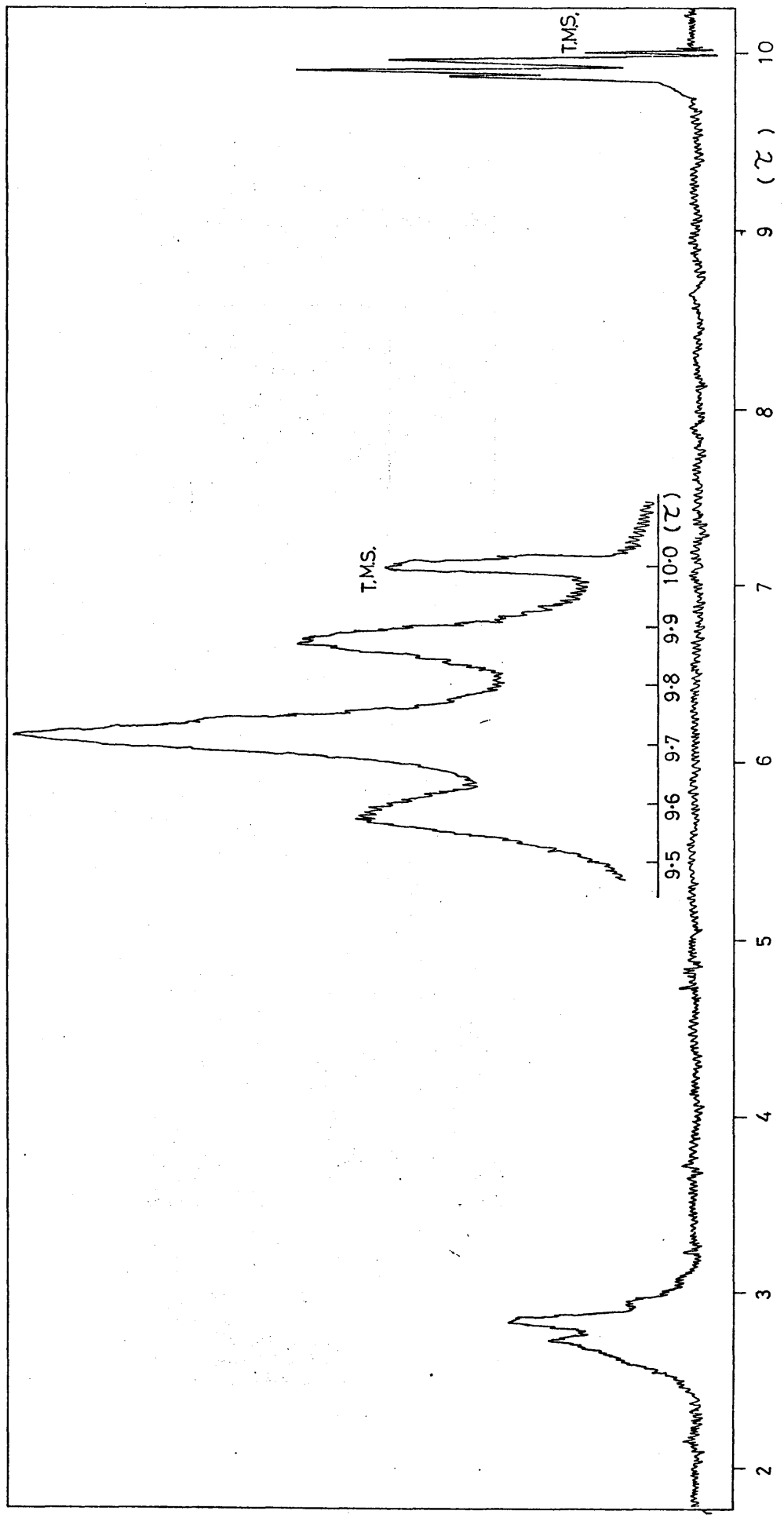


Fig. 3.1 NMR SPECTRUM OF POLY(METHLYPHENYLSILOXANE)

FIGURE 3.2

TGA Curves for Hydroxyl-ended PMPS

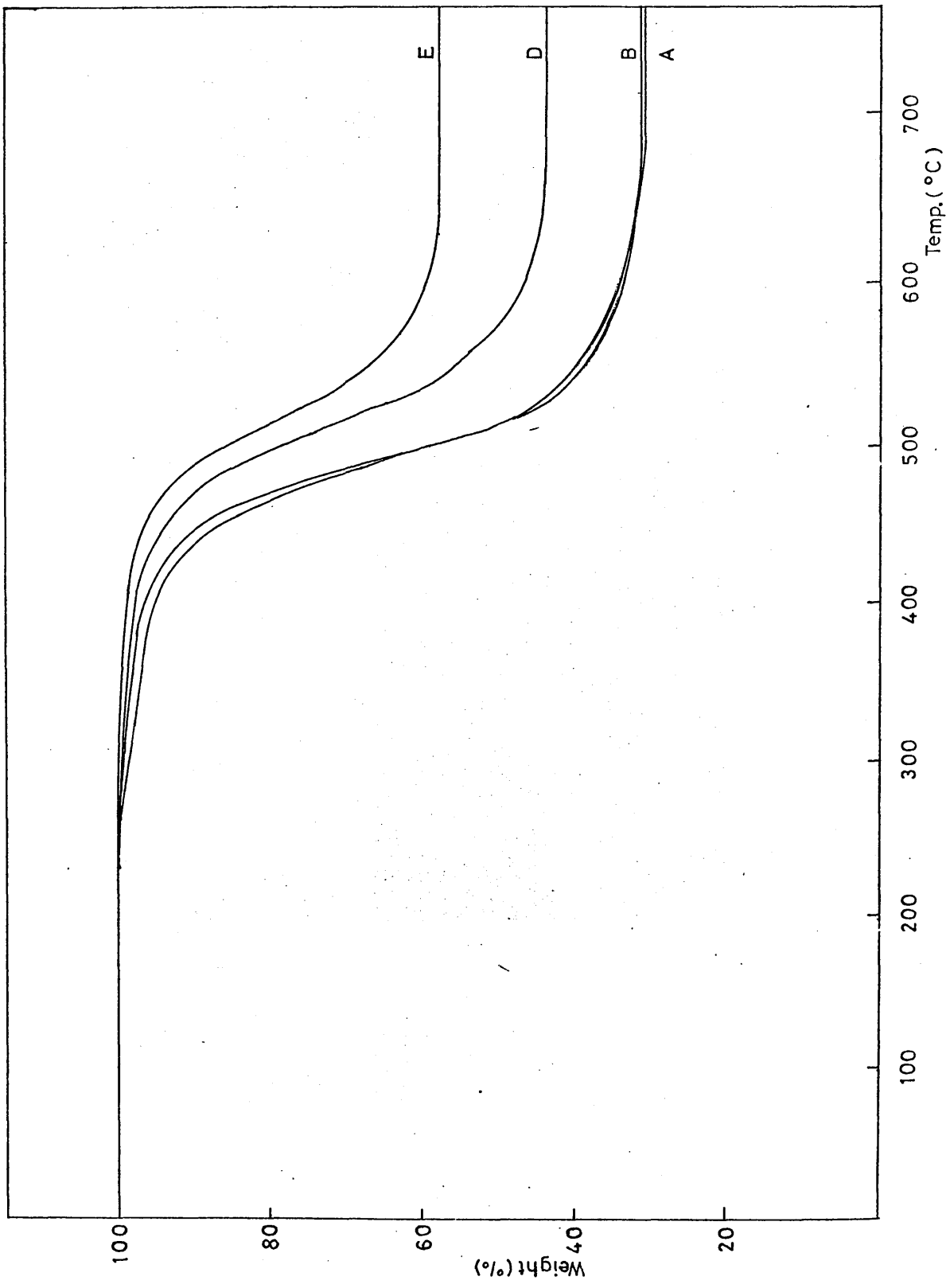
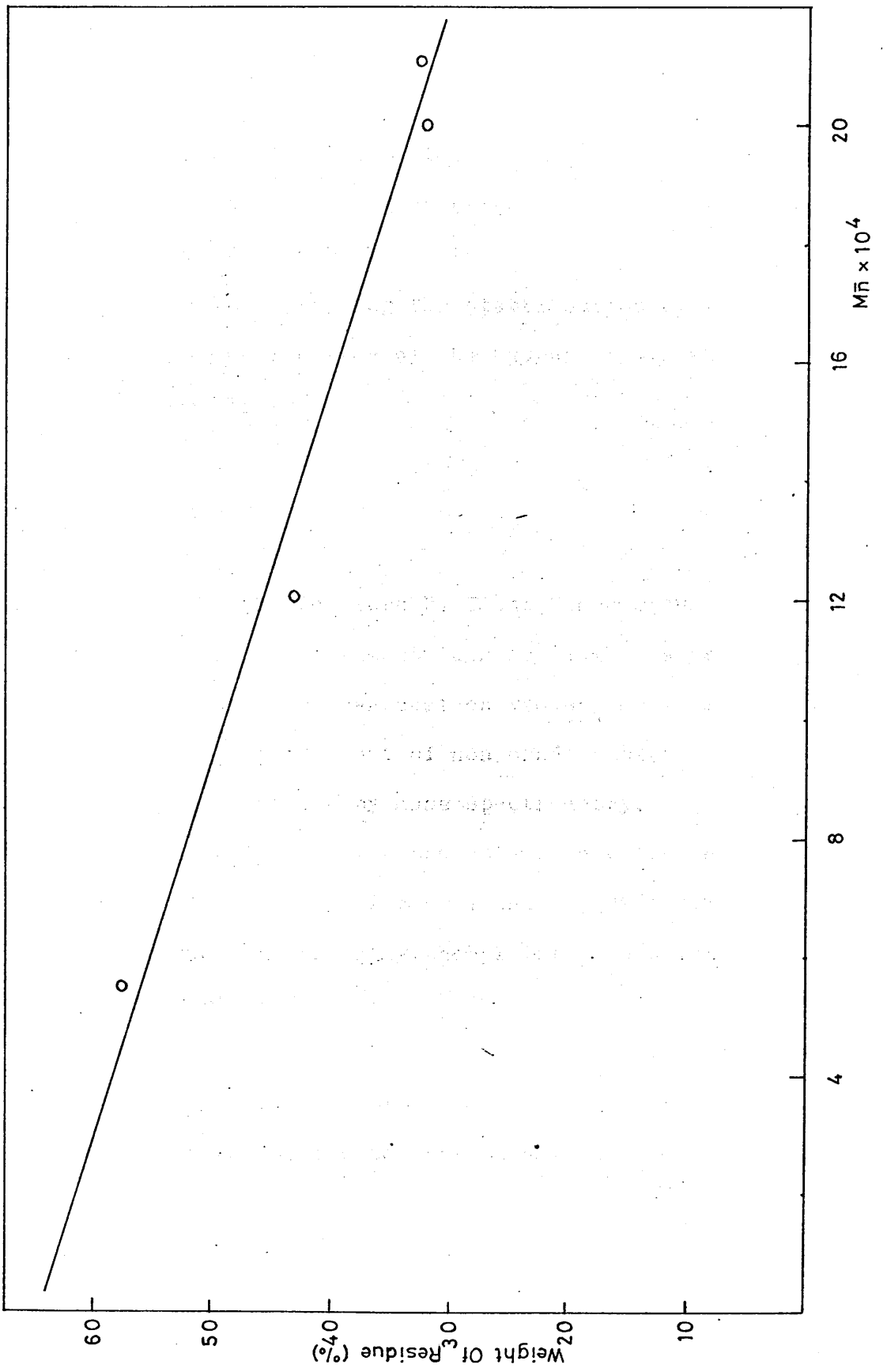


FIGURE 3.3

Plot of % Weight of Residue from TGA vs Initial Molecular Weight for Hydroxyl-ended PMPS



residue of the above polymers versus their molecular weights. It can clearly be seen that the stability of polymers with hydroxyl end groups (as measured by weight of residue) is inversely proportional to their molecular weight.

TGA traces of the end-blocked polymers and their hydroxy terminated analogues (Figure 3.4) show the end-blocked polymers to be less stable.

A mechanism involving the stabilisation of these polymers by the reaction of the hydroxy chain ends will be discussed later.

3.5 T.V.A.

TVA traces of polymers B, C and E are shown in Figure 3.5, all three being almost identical. IR analysis of the volatile products of degradation showed small amounts of benzene. The trace amount of non-condensable material was identified as methane by mass spectrometry.

The major degradation products were collected as the cold ring fraction. Analysis of this by NMR showed the major products to be methylphenyl trimer and tetramer isomers (Table 3.3).

It can be seen that, due to the small amounts of products volatile at ambient temperature obtained from these polymers and due to their stability under these conditions, TVA is of limited use in this study.

FIGURE 3.4

TGA Curves for Hydroxyl and Trimethylsiloxy-ended PMPS

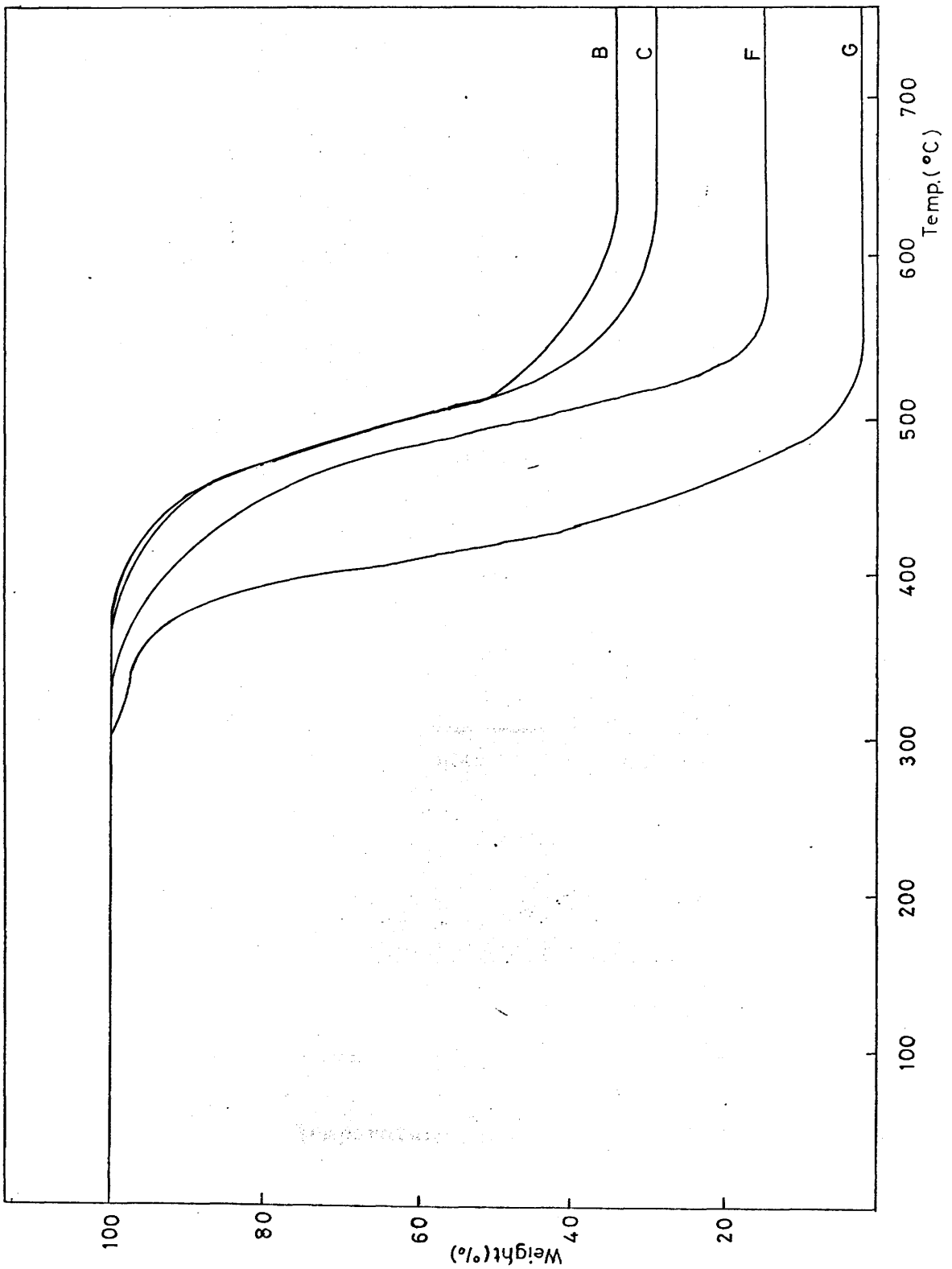
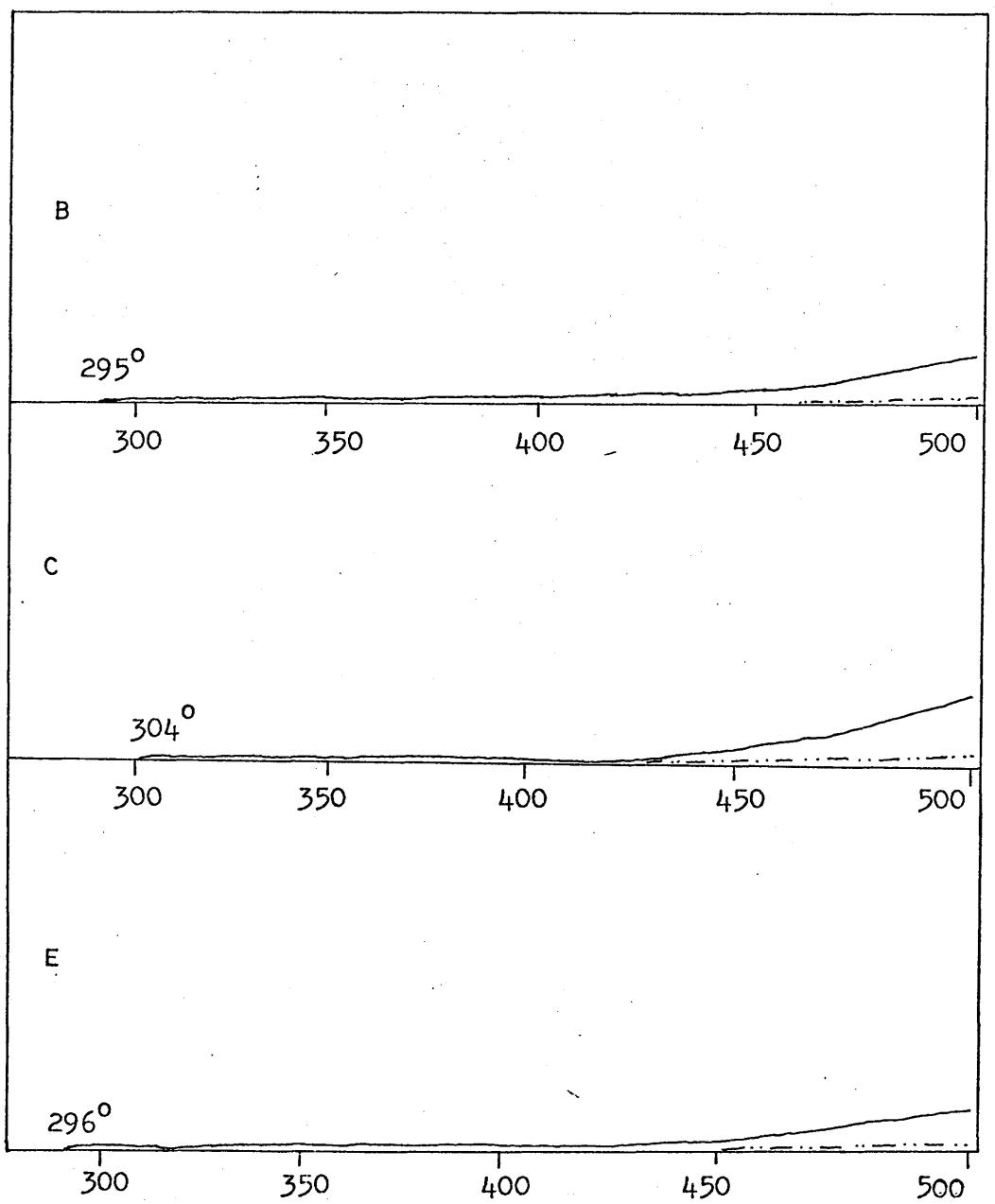


FIGURE 3.5

TVA Curves for Hydroxyl and Trimethylsiloxy-ended PMPS



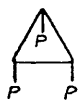
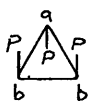
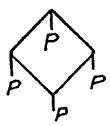
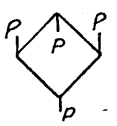
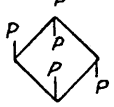
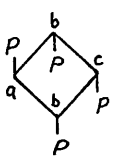
Trap Temperature °C

—— 0, -45, -75, -100 (all co-incident)

·-·-· -196

TABLE 3.3

Analysis of Cold Ring Fraction

Structure of possible degradation product	Methyl Proton* Shift (τ)	Observed Shift (τ)	Difference (τ)
	9.484	9.488	+0.004
	a)9.622 b)9.557	9.623 9.562	+0.001 +0.005
	9.519	9.525	+0.006
	9.743	9.743	0.000
	9.719	9.721	+0.002
	a)9.852 b)9.608 c)9.958	9.850 9.600 9.592	-0.002 -0.008 -0.006

*Ref: 40

3.6 Vacuum Line Degradation System

This system, as described earlier, was used extensively to study the degradation reactions of these polymers.

It was designed to allow easy collection of the major degradation products and to follow the evolution of benzene and weight loss from the samples heated isothermally over a range of temperatures.

(i) Isothermal weight loss under vacuum

Data for weight loss at 300°C, 400°C, 450°C and 500°C for polymers B, C and E are given in Table 3.4.

Consistant with data from TGA studies, the lower molecular weight polymer, E, shows a lower weight loss at all temperatures than the polymer with higher molecular weight (B).

Polymer C, the end-blocked analogue of polymer B, has a smaller weight loss than polymer B at all temperatures. This is not consistent with data from TGA studies.

(ii) Analysis of products

(a) Benzene evolution

The evolution of benzene at various temperatures was followed quantitatively for polymers B, C, D and E and the results are shown in Table 3.5.

For the hydroxy ended polymers, the amounts of benzene formed at all temperatures are less the greater the molecular weight.

TABLE 3.4

Isothermal Weight Loss (%) from PMPS

Polymer	300°C	400°C	450°C	500°C
B	5.8	89.3	90.0	82.1
C	1.0	83.3	86.1	75.9
E	4.7	85.5	87.7	79.3

TABLE 3.5

Moles of Benzene Evolved / g. of Polymer ($\times 10^{-5}$)

Polymer	300°C	400°C	450°C	500°C	Theoretical Hydroxy Yield
E	0.80	7.76	47.09	156.24	3.59
D	-	-	-	101.67	1.65
B	0.74	6.05	33.71	94.17	0.94
C	0.00	13.48	39.59	121.98	0.00

Polymer C produces more benzene than its hydroxy ended analogues at 400°C and above but does not give any benzene at 300°C.

The last column in Table 3.5 gives the amount of benzene that would be evolved if every hydroxy chain-end group reacted to give one molecule of benzene.

Trace amounts of benzene have been detected at temperatures as low as 150°C, with the loss of polymer solubility in known solvents.

(b) Analysis of 'cold-ring' fraction

A Qualitative Analysis

NMR This is the most convenient method for general analysis of the products but it was of limited use for the identification of all the minor products. A typical spectrum with the methyl shift region expanded, is shown in Figure 3.6.

GLC Conditions for separating mixtures of methylphenyl trimer and tetramer isomers were established - a typical GLC trace is shown in Figure 3.7

From the GCMS trace of the degradation products (Figure 3.8), it can be seen that there are three peaks (C, H and I) in addition to those from the known isomers. These peaks were identified by GCMS.

GCMS This technique was used to confirm the structure of the two trimer and four tetramer isomers and to aid the identification of the three unknown peaks. The mass spectra of all nine compounds are shown in Figure 3.9.

FIGURE 3.6

NMR Spectrum of Degradation Products from PMPS

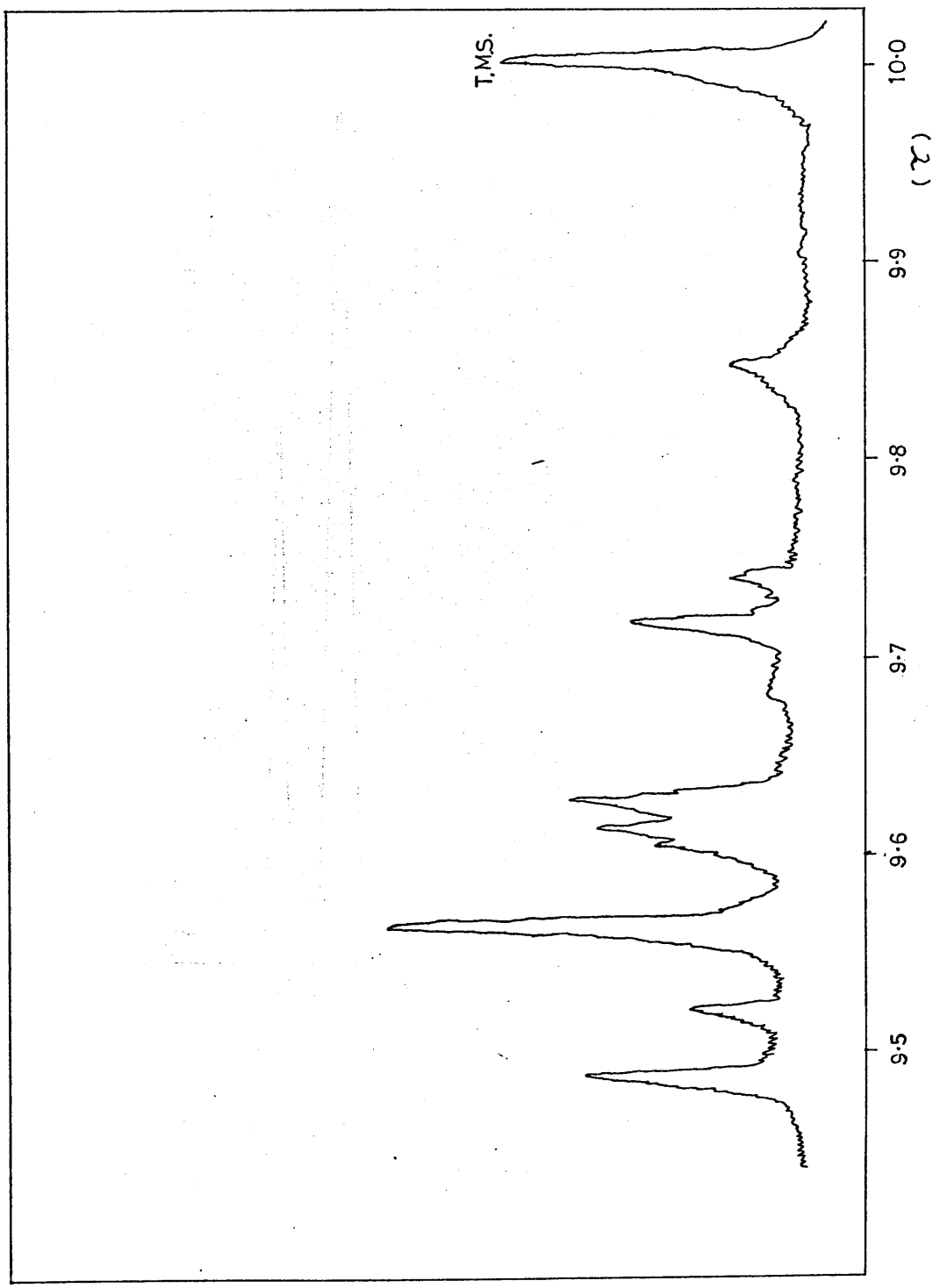


FIGURE 3.7

GLC Trace of Methylphenyl Trimer and Tetramer Cyclics

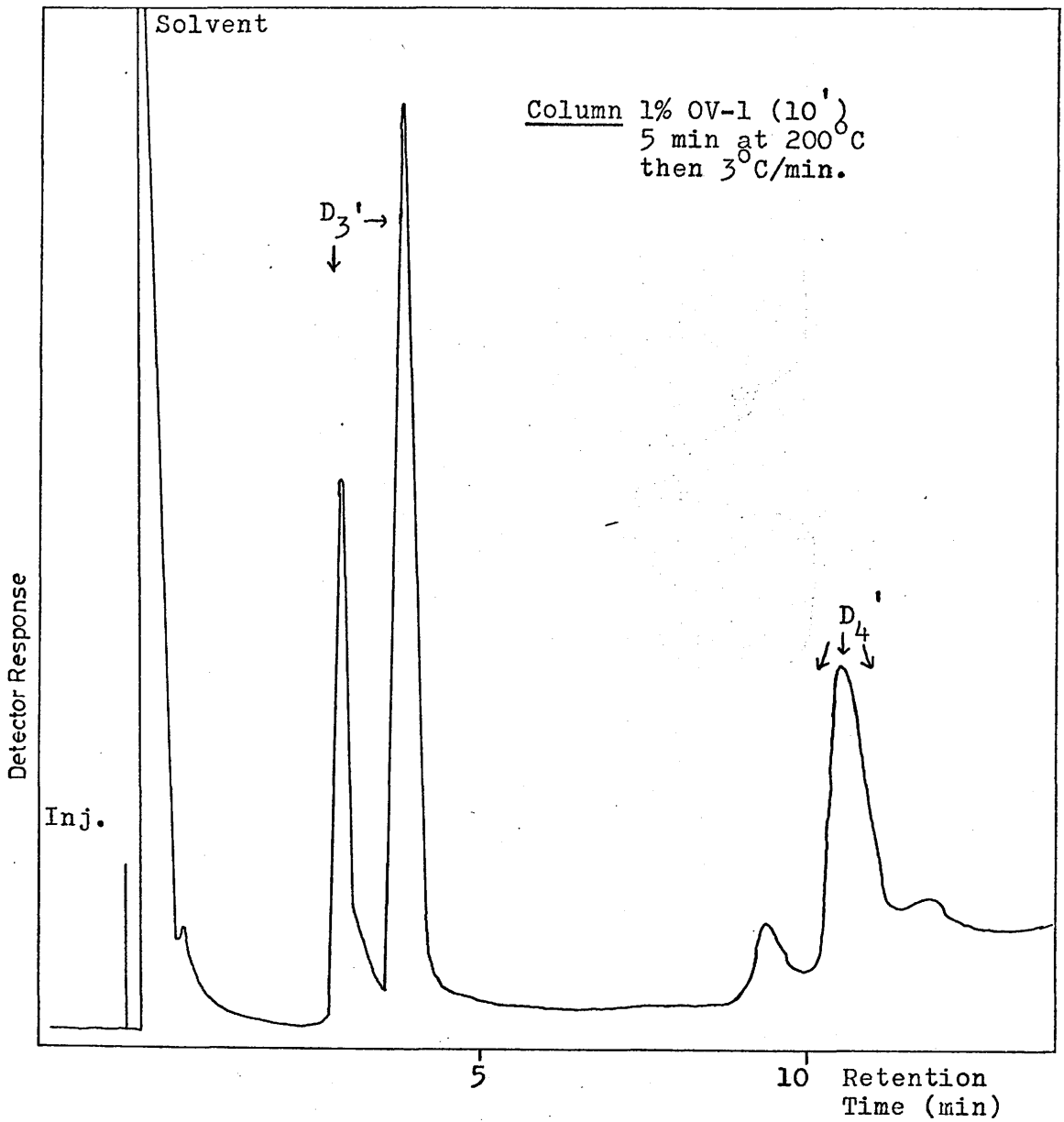
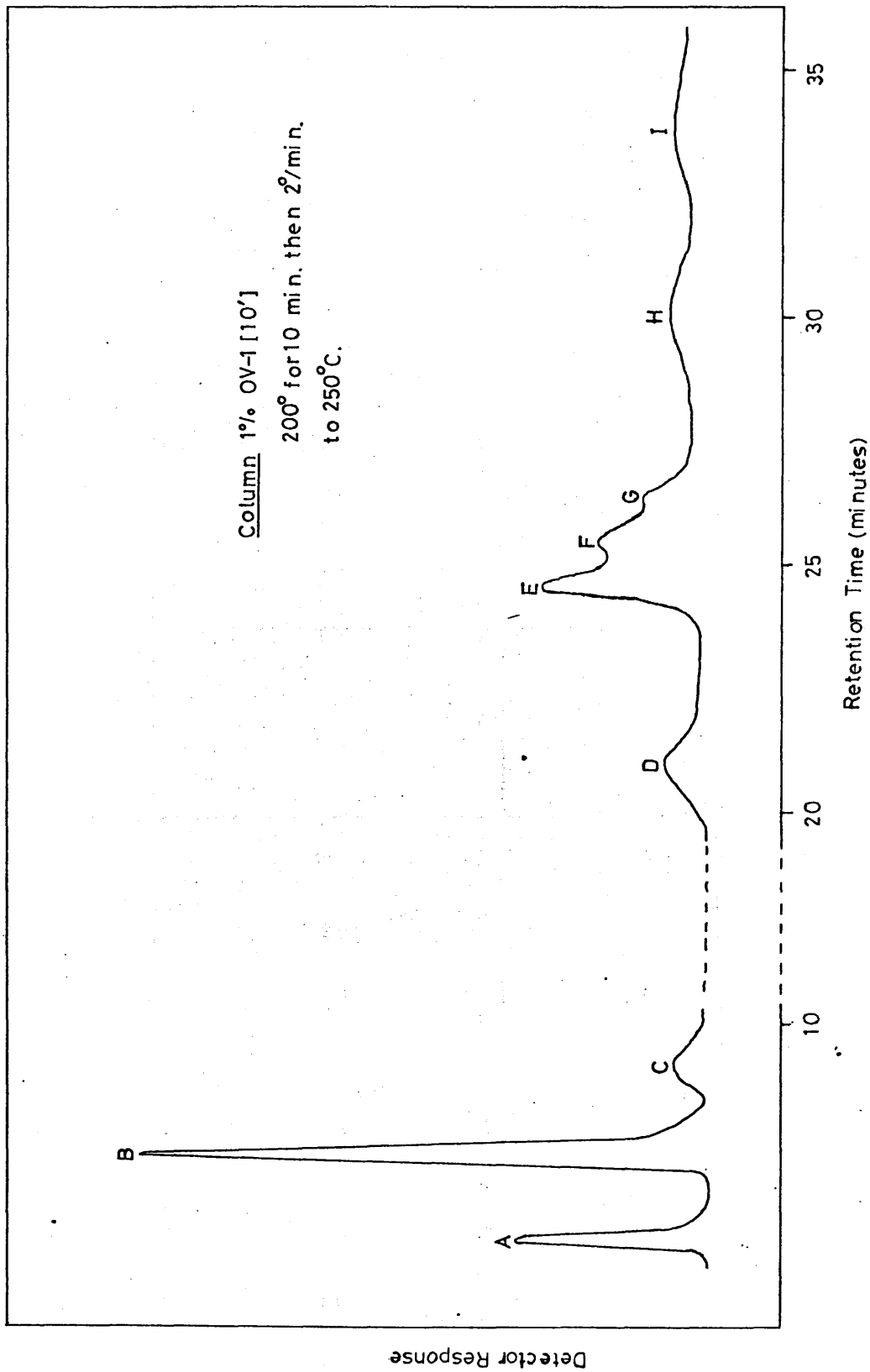


FIGURE 3.8

GCMS Trace of Degradation Products



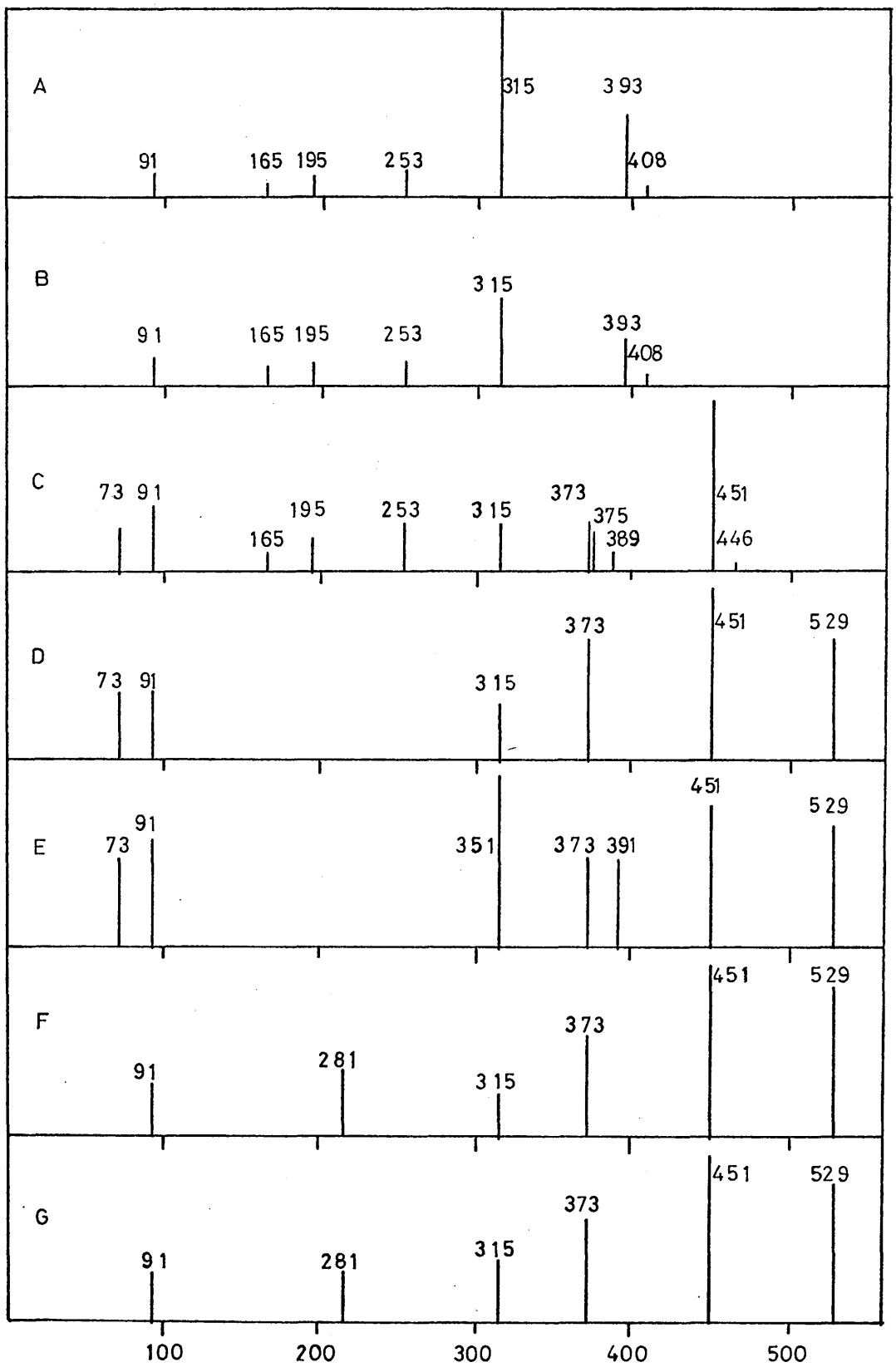

A
315
393
91
165
195
253
408
B
315
91
165
195
253
393
408
C
73
91
195
253
315
373
451
165
375
389
446
D
373
451
529
73
91
315
E
451
529
91
73
351
373
391
F
451
529
373
91
281
315
G
451
529
373
91
281
315
100
200
300
400
500

FIGURE 3.9 (a)

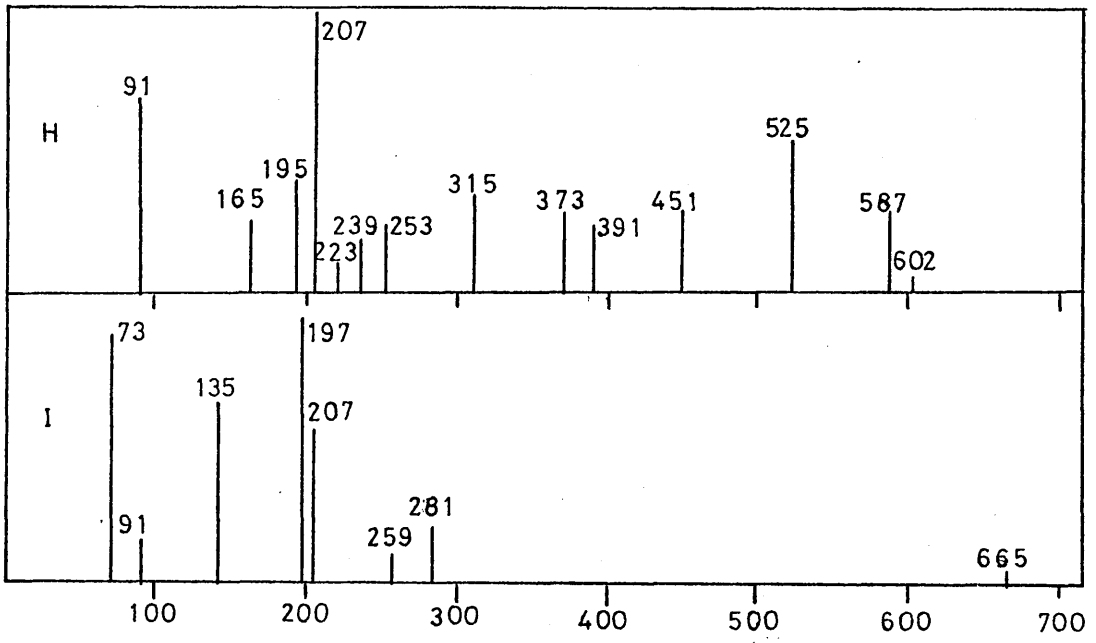
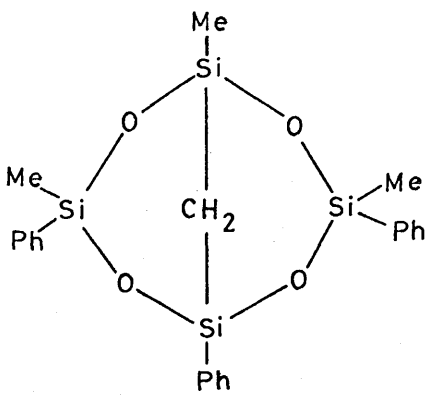


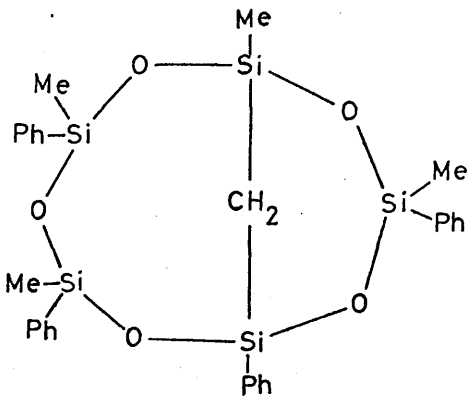
FIGURE 3.9 (b)

Mass Spectra from GCMS of Degradation Products of PMPS

It is proposed that peak I is due to the cyclic pentamer isomer and that peaks C and H have the following structures:



C



H

A mechanism leading to the production of these compounds will be discussed later.

The only other structure which would have the appropriate m/e values for compounds C and H are ones in which the meth/ylene bridges are replaced by phenylene bridges. No distinction between the two possible types can be drawn from GCMS data for this polymer system, but evidence will be presented in later Chapters which will suggest that the structures with the methylene bridges are correct.

B Quantitative Analysis

The quantitative analyses (by GLC) of the cyclics formed from the degradation of polymers B, C and E at 300°C, 400°C and 500°C are shown on Table 3.6, 3.7 and 3.8. The analyses were carried out as described in Chapter 2 using the 'Normalisation' method. The Rf values for those compounds which could not be isolated were estimated from the known Rf values.

There is no significant difference in the amounts of the various cyclics produced from the high (polymer B) and low (polymer E) molecular weight polymers at each temperature. Polymer C (the end-blocked analogue of polymerB) shows a similar distribution of products to polymers B and E, except at 300°C where no cyclics were detected.

The relative amounts of the cyclics formed above 400°C change little with temperature, but at 300°C the amounts of the higher cyclics, D_5' and D_4' increase sharply at the expense of D_3'. The bicyclic compounds C and H are only found at 450°C and 500°C.

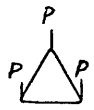
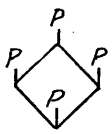
3.7 Discussion

The major degradation products of polysiloxanes are cyclic compounds. Three mechanisms have been postulated to account for their formation.

TABLE 3.6

Quantitative Analysis of Degradation Products (% Weight)

Polymer B

Compound	300°C	400°C	450°C	500°C
	6.4	17.8	18.7	17.1
	19.8	48.8	52.8	48.0
C*	-	-	<1.0	3.1
	4.3	3.6	3.1	3.8
D_4'isomers	40.6	24.6	19.6	22.5
H*	-	-	-	<1.0
D_5'	27.9	5.2	5.5	4.8

* Structure given earlier

TABLE 3.7

Quantitative Analysis of Degradation Products (% Weight)

Polymer C

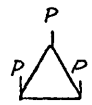
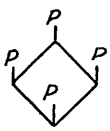
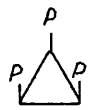
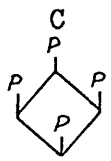
Compound	300°C	400°C	450°C	500°C
	-	11.3	15.1	17.3
	-	49.3	44.1	43.9
C	-	-	<1.0	1.6
	-	5.2	5.3	5.7
D_4' isomers	-	27.6	28.1	24.9
H	-	-	2.0	<1.0
D_5'	-	6.7	4.9	5.3

TABLE 3.8

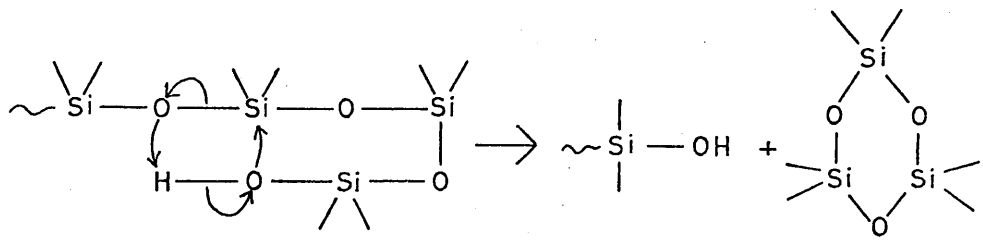
Quantitative Analysis of Degradation Products (% Weight)

Polymer E

Compound	300°C	400°C	450°C	500°C
	5.3	20.4	16.5	15.7
	16.0	51.2	46.5	43.8
	-	-	<1.0	2.7
	5.4	3.6	4.3	4.6
D_4' isomers	40.0	21.5	26.4	23.6
H	-	-	<1.0	1.5
D_5'	33.3	3.1	5.4	8.1

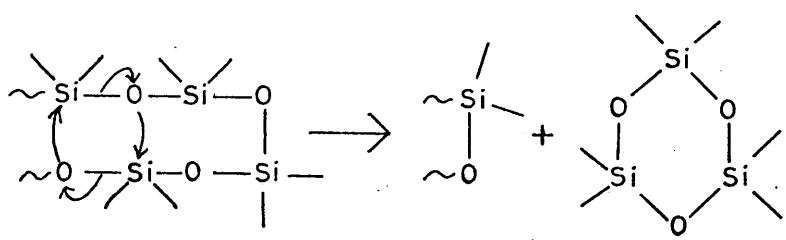
(i) Depolymerisation from chain ends

Cyclic products are formed by an intramolecular reaction involving the hydroxy end groups (Refs: 17, 22)



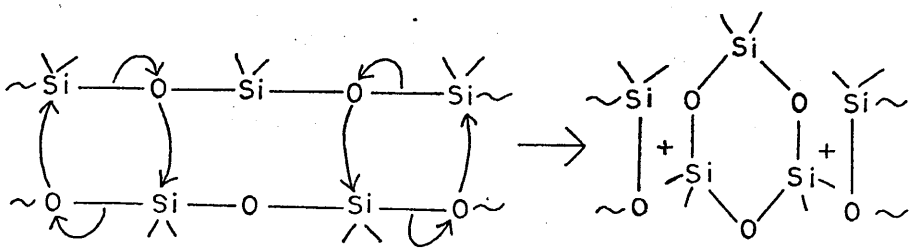
(ii) Depolymerisation by random elimination

This is an intramolecular rearrangement thought to be favoured by the spiral structure of siloxane chains (Refs: 19, 34)

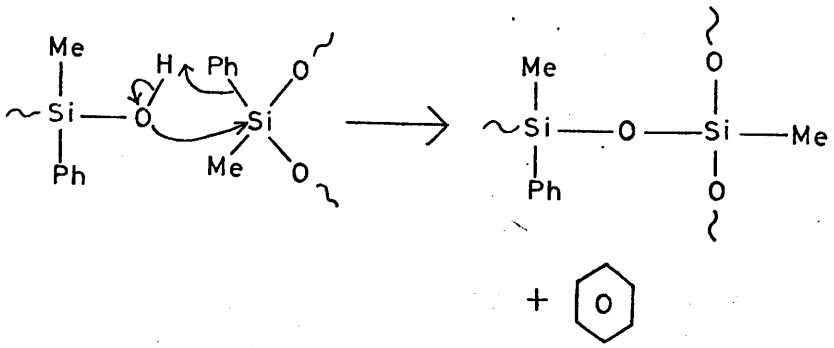


(iii) Depolymerisation by intermolecular rearrangement

It is believed (Ref: 26) that an intermolecular reaction similar to (ii) can also occur.



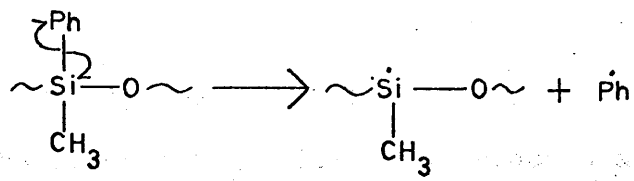
Macfarlane (Ref: 20) has shown reaction (i) to be very important in the degradation of polydimethylsiloxanes. End blocking of this polymer gives a more stable sample (as measured by rate of weight loss by TGA) whereas end blocking of polymethylphenylsiloxane gives a less stable sample. It is proposed, therefore, that the hydroxyl chain end is involved in a stabilisation reaction of the following type:



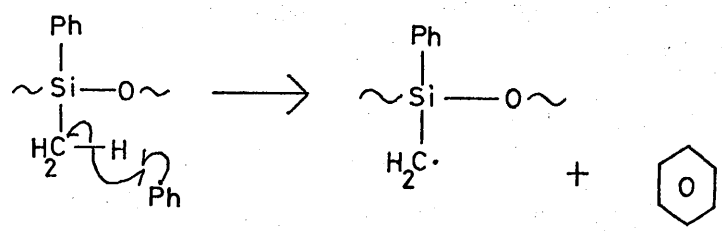
Clearly the amount of benzene formed would be a function of molecular weight - the lower the molecular weight, the more benzene would be produced. The weight of the residue would also be a function of molecular weight. The lower the molecular weight, the greater the number of cross-links and thus the greater the amount of residue.

At 300°C, the amounts of benzene produced agree well with the yields predicted from the number of hydroxy end groups. Above 300°C, however, the amounts produced are too large to be formed from the chain-end reaction alone, so clearly another mechanism must be involved.

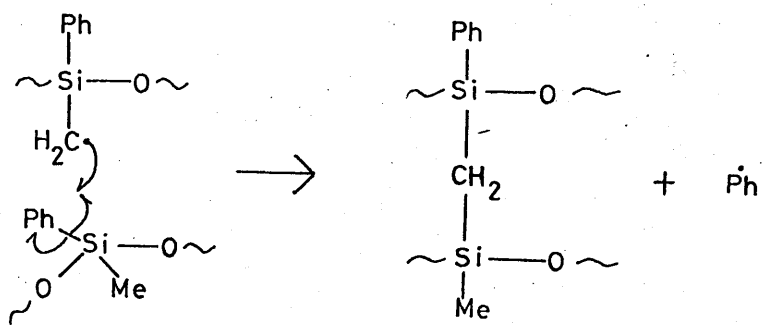
Sobolevskii et al (Ref: 28) have proposed a mechanism forthe thermal rearrangement of oligomethylphenylsiloxanes involving the homolytic fission of the Si-Ph bond. A similar mechanism is therefore proposed for the production of benzene which was observed at 400°C and above.

a) 

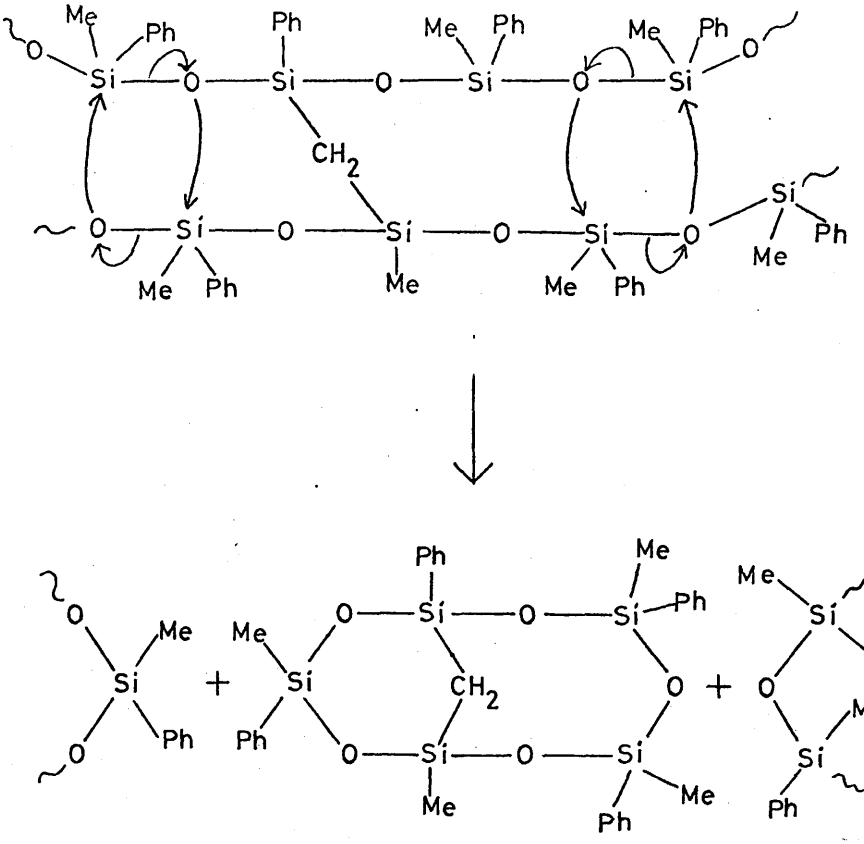
b)



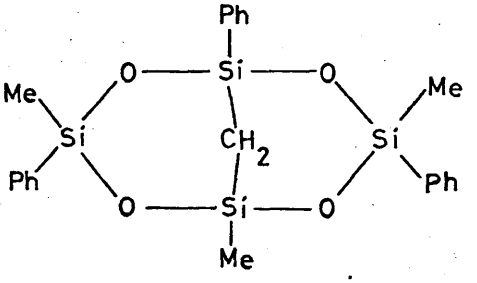
c)



Once the methylene bridge has been formed between two chains, subsequent degradation might proceed as follows:

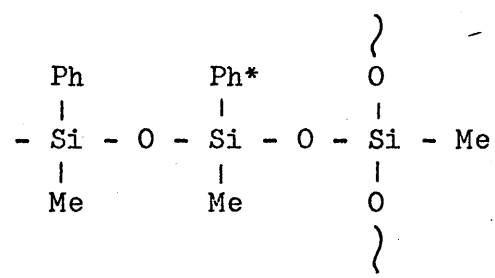


And similarly, to produce

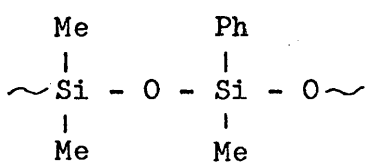


The GCMS data described earlier in the Chapter of the degradation products are consistent with the appearance of these bicyclic compounds.

The amount of benzene formed by the above mechanism should be independent of the molecular weight of the degrading polymer but in practice this is not the case. The evolution of benzene at higher temperatures is still found to be inversely proportional to molecular weight. This is thought to be due to the increased lability of the phenyl group (*) adjacent to the cross-link formed by the hydroxy chain end.



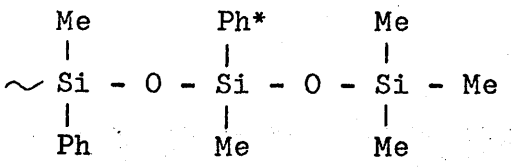
Andrianov (Ref: 54) has proved that a phenyl group, in an electronically unsymmetrical environment, that is



is more labile than otherwise.

The low molecular weight polymer would have a larger number of these labile groups and would thus evolve more

benzene. The large quantities of benzene evolved from the end-blocked polymers are also thought to arise from the labile phenyl groups (*) next to the trimethylsilyl end group i.e.



CHAPTER 4

Poly(dimethyl/methylphenylsiloxane)

4.1 Introduction

The work described in this Chapter relates to the preparation and thermal degradation of linear siloxane copolymers containing varying ratios of dimethyl to methylphenyl units. These copolymers were prepared by polymerising 'mixed' cyclics, i.e. cyclic siloxanes containing both dimethyl and methylphenyl units, hopefully to give copolymers with regular repeat units along the chain.

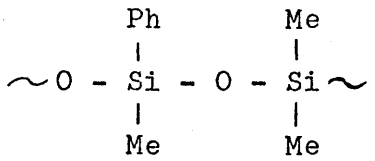
Andrianov and Yakushkina (Ref: 58) first gave details of the preparation of heptamethylphenylcyclotetrasiloxane (D_3D_1') and later (Ref: 59) D_2D_2'. They demonstrated that both could be converted to high polymers using an acid catalyst but that cleavage of the Si-Ph bond occurred with catalyst concentrations greater than 2%.

In 1966, Andrianov et al (Ref: 51) when comparing the rate of polymerisation of tetramers D_3D_1', D_2D_2', D_1D_3' and D_4' found that the rate decreased with increasing phenyl content and that only the first three tetramers would form high molecular weight polymers (using 0.5% KOH as catalyst at 150°C).

Cyclics D_3D_1', D_2D_2' and D_1D_3' also underwent a cross-linking reaction caused by rupture of the Si-Ph

bond. They also discovered, however, that octamethyl/cyclotetrasiloxane was less reactive than D_3D_1', D_2D_2' and D_1D_3' which is clearly contrary to the above trend. They claimed that this was due to two opposing factors: a) the electron withdrawing phenyl groups would increase the $\delta+$ charge on that silicon atom making it more liable to nucleophilic attack, and b) that increasing phenyl content would cause greater steric hindrance shielding the siloxane from nucleophilic attack by the $OH^{\ominus}$ ion.

Later work by Andrianov et al (Refs: 54, 60, 61) demonstrated that the chain transfer reaction undergone by mixed dimethyl and methylphenyl polysiloxanes depended on the increased lability of phenyl radicals in the following structure:



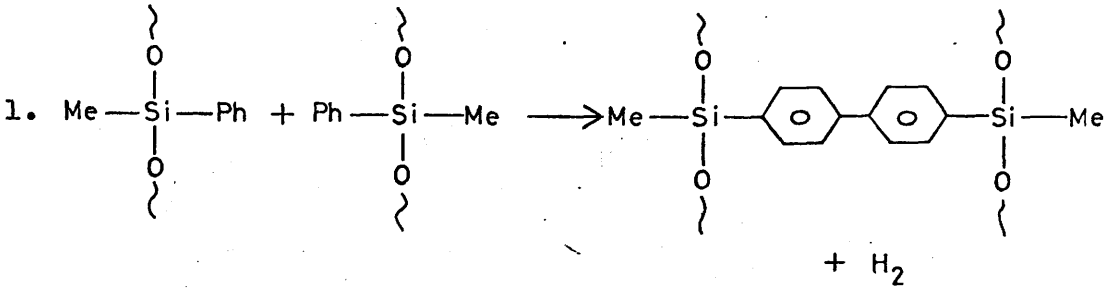
due to the non-uniformity of the electron distribution over the molecular chain.

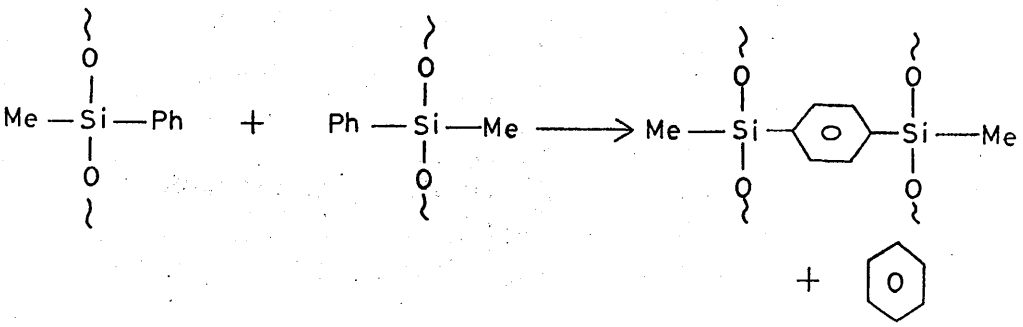
These workers also studied the rate of polymerisation of cyclic siloxanes in the presence of 0.1% KOH and how it was affected by the electronegativity of the organic substituents and by the addition of aprotic solvents such as dimethyl formamide and dimethyl sulphoxide. They concluded that electron donating groups lowered the rate of polymerisation whereas electron withdrawing groups accelerated it because the latter made the silicon more

liable to nucleophilic attack. Aprotic solvents were shown to increase the rate of anionic polymerisation as a result of better separation of the catalyst ion pair.

Kuznetsova et al (Ref: 62) isolated and characterised a range of mixed dimethyl and methylphenyl cyclics (from trimer to tetramer) obtained from the vacuum distillation of mixtures prepared from the condensation of Me_2SiCl_2 and $MePhSiCl_2$ and from the products of thermocatalytic degradation of polydimethyl/methylphenyl siloxanes.

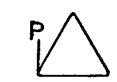
More recently, Skorokhodov et al (Ref: 63) have degraded samples of polydimethyl/methylphenyl siloxane under vacuum and have found 'mixed' cyclics (trimer to tetramer) as the products at 400°C. At higher temperatures (500°C), they have observed the evolution of hydrogen and benzene which are accounted for in the following mechanisms:



2. 

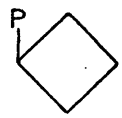
4.2 Preparation of Dimethyl/methylphenyl 'Mixed' Cyclics

Cyclic siloxanes containing both dimethyl and methylphenyl siloxane units were synthesised as described in Chapter 2. The cyclic compounds prepared were:

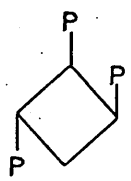


D_2D_1'

D_1D_2'



D_3D_1'



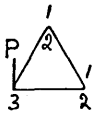
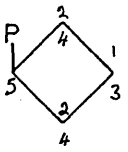
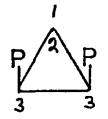
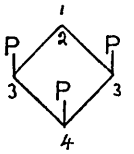
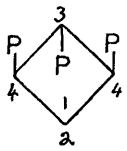
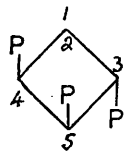
+ isomers

D_1D_3'

These were characterised as detailed in Table 4.1 and their purity (> 99.9%) was checked by GLC. It was not

TABLE 4.1

Characterisation of Dimethyl/methylphenyl 'Mixed' Cyclics

Isomer Structure	Mass Spec (m/e Parent Ion)	NMR (τ-Methyl Protons) Obs.	Lit.*	B Pt (°C/mmHg) Obs.	Lit.
	284(M+)	1. 9.873 2. 9.785 3. 9.633	1. 9.875 2. 9.786 3. 9.636	68°/1.5	94°/6 (Ref:62)
	280(M-78)+	1. 9.955 2. 9.955 3. 9.890 4. 9.845 5. 9.690	1. 9.949 2. 9.949 3. 9.887 4. 9.844 5. 9.688	75°/0.1	108°/5.0 (Ref:40)
	346(M)+	1. 9.872 2. 9.724 3. 9.568	1. 9.879 2. 9.726 3. 9.566	130°/1.0	122-124°/0.5 (Ref:62)
	482(M)+	1.10.053 2. 9.760 3. 9.577 4. 9.537	1.10.054 2. 9.758 3. 9.578 4. 9.534	178-179°/0.6	167-171°/0.05 (Ref:50)
		1. 9.945 2. 9.805 3. 9.790 4. 9.683	1. 9.959 2. 9.803 3. 9.782 4. 9.693		
		1. 9.923 2. 9.838 3. 9.778 4. 9.675 5. 9.652	1. 9.935 2. 9.844 3. 9.782 4. 9.670 5. 9.648		

* Ref: 50

possible to separate the individual isomers of D_1D_3'.

4.3 Preparation of Polydimethyl/methylphenyl Siloxanes

Five hydroxy ended copolymers with varying ratios of dimethyl:methylphenyl units were prepared along with three trimethylsilyl end-blocked copolymers. The polymerisations were carried out as described in Chapter 2 - the reaction conditions and number average molecular weights of the copolymers prepared are shown in Table 4.2. The percentage phenyl content of each copolymer is also shown.

Attempts to define the microstructure of the copolymers by ^1H NMR proved impossible due to the complexity of the methyl proton resonances.

4.4 T.G.A.

TGA traces for the hydroxy ended copolymers and for the end-blocked copolymers with their hydroxy ended analogues are shown on Figures 4.1 and 4.2 respectively.

The stability of the hydroxy ended copolymers (as measured by % weight of residue) is seen to increase with % phenyl content of the copolymer. Copolymer C, and to a lesser extent copolymer E, do not fit into this general trend- reasons for this will be discussed later.

Comparison of the hydroxy and end-blocked samples shows that only the end-blocked analogue of copolymer A is more stable than the hydroxy ended copolymer. For copolymers C and D, and G and H, the hydroxy ended copolymer is more stable.

TABLE 4.2

Preparation of Polydimethyl/methylphenyl Siloxanes

Copolymer	Monomer	Polymerisation Temp. (^{o}C)	Catalyst Concn.(w/w%)	$\bar{M}n$	% Phenyl Content
A	$D_3D_1'+D_4$	120	0.1	236000	6.25
B	End-blocked sample of Copolymer A			236000	6.25
C	D_3D_1'	120	0.1	272000	12.50
D	End-blocked sample of Copolymer C			272000	12.50
E	D_2D_1'	120	0.1	64000	16.67
F		120	0.1	153000	33.33
G	D_1D_3'	120	0.1	50300	37.33
H	End-blocked sample of Copolymer G			50300	37.33

FIGURE 4.1

TGA Traces of Dimethyl/methylphenyl Copolymers

(Hydroxy Ended Samples)

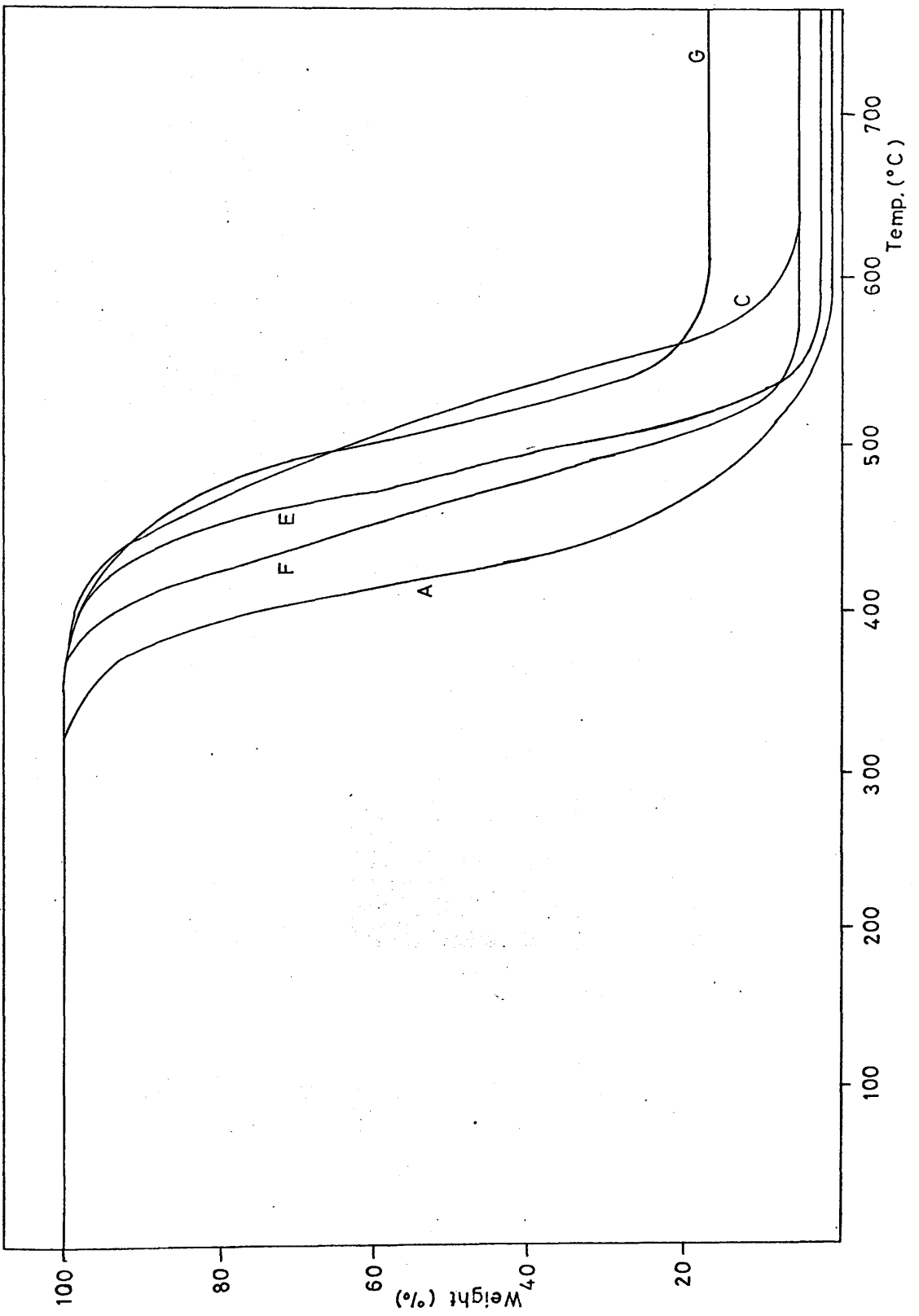
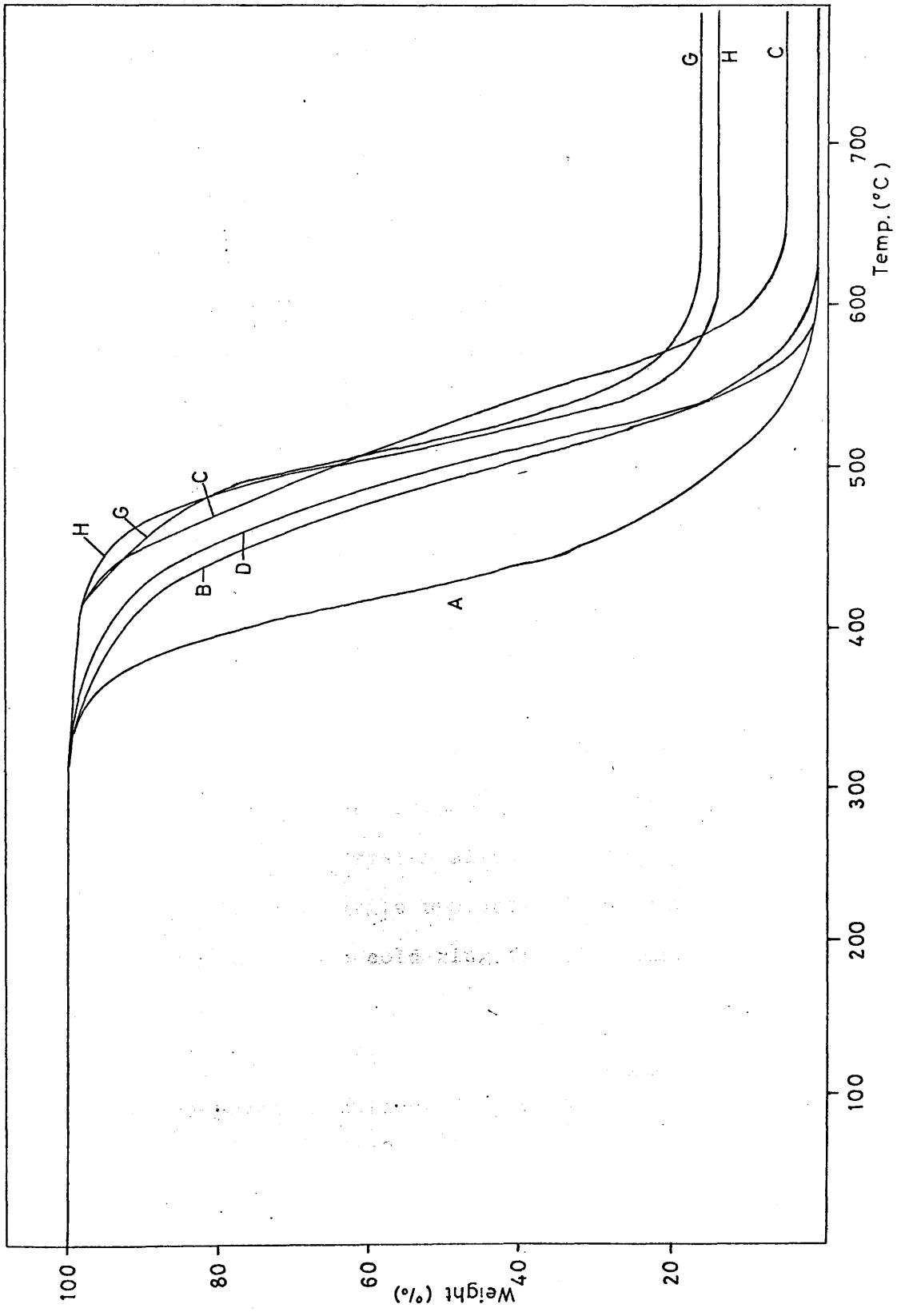


FIGURE 4.2

TGA Traces of Dimethyl/methylphenyl Copolymers

(Hydroxy and End-blocked Samples)



4.5 T.V.A.

TVA traces for the dimethyl/methylphenyl copolymers are shown on Figure 4.3.

The condensable volatile products were shown, by IR analysis, to be made up of small amounts of benzene from all of the copolymers and larger amounts of hexamethylcyclotri/siloxane and octamethylcyclotetrasiloxane from all the copolymers except F,G and H. NMR analysis of the cold-ring fraction showed it to be a complex mixture of dimethyl/methylphenyl cyclic compounds.

Because the TVA unit can only operate up to 500°C, which is below the temperature of maximum rate of degradation of most of these copolymers, no conclusions can be drawn about stability trends.

4.6 Vacuum Line Degradation System

This system was used to study the degradation properties of copolymers at 300°C and 500°C.

The design of the system allows for the quantitative collection of the volatile products (i.e. benzene, D_3 and D_4) as well as the cold-ring fraction. The first trap, at -70°C, condenses out the D_3 and D_4 cyclics so that they may be recovered with the rest of the cyclic degradation products collected from the cold finger. The second trap, at -196°C, condenses out any benzene formed which can then be distilled into a previously

FIGURE 4.3 (i)

TVA Traces of Dimethyl/methylphenyl Copolymers

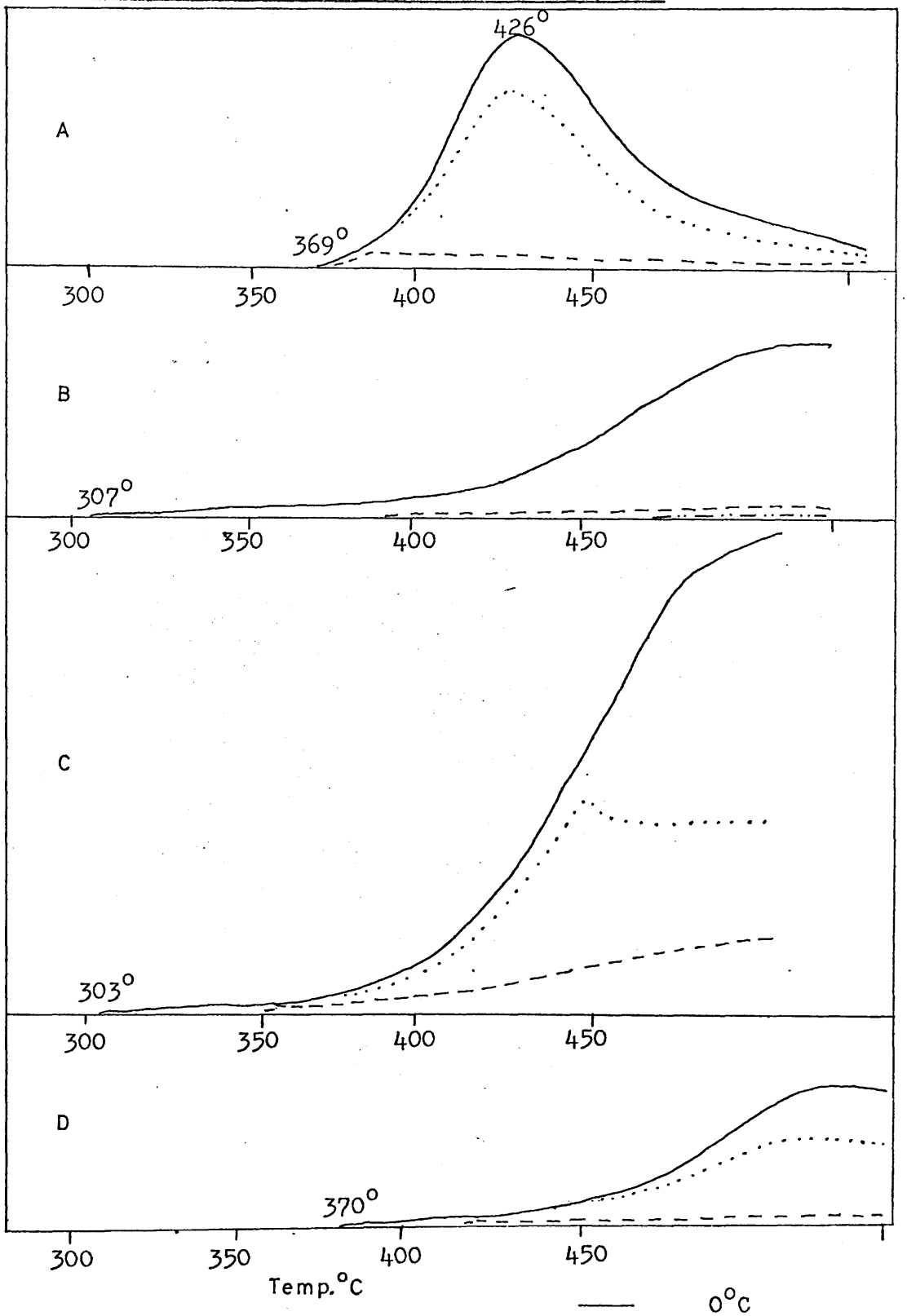
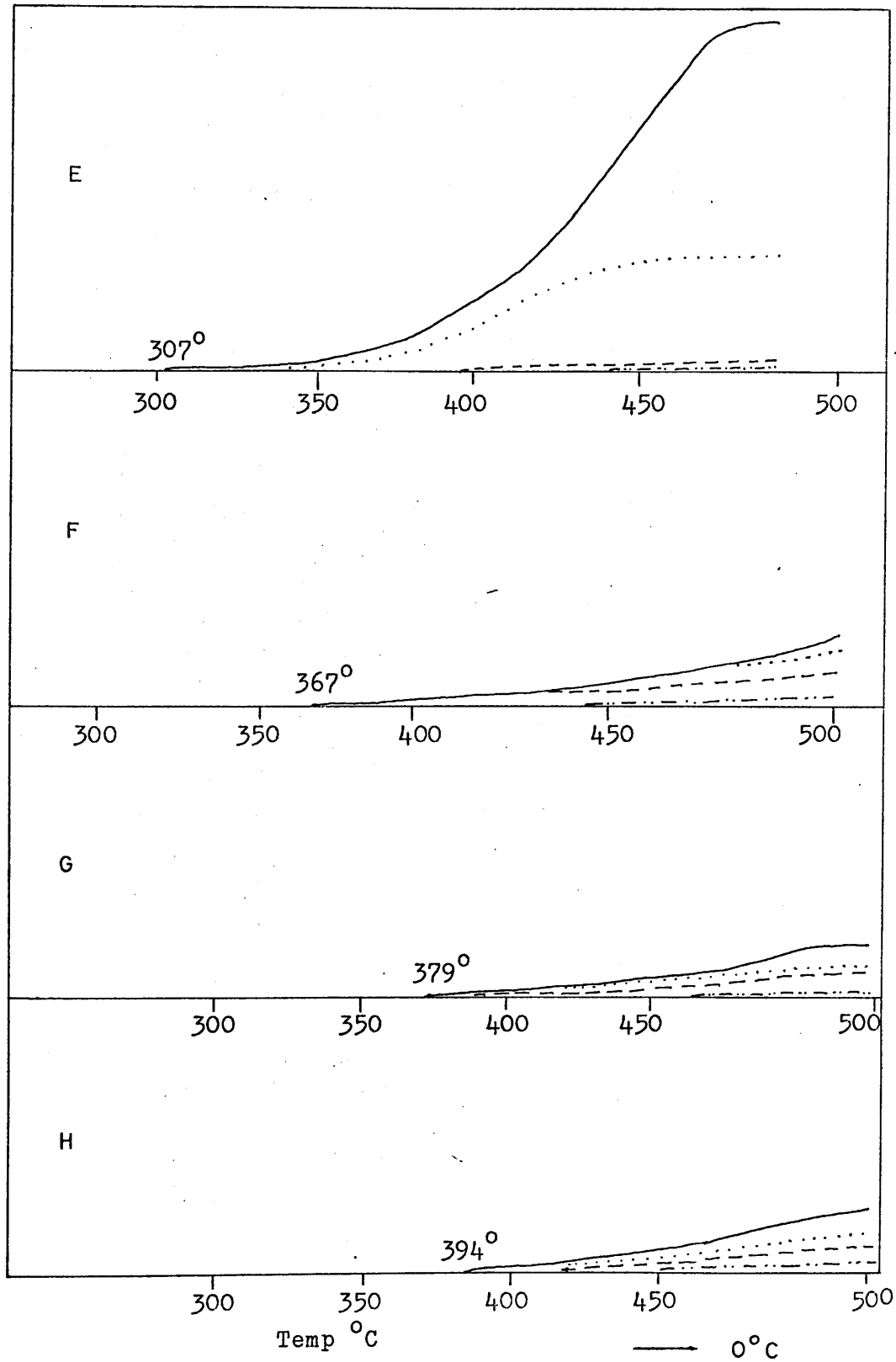


FIGURE 4.3 (ii)

TVA Traces of Dimethyl/methylphenyl Copolymers



calibrated gas-cell and quantitatively estimated.

(i) Isothermal weight loss under vacuum

Data for weight loss at 500°C for the hydroxy ended polymers are shown on Figure 4.4 (i). As from TGA, it can be seen that the stability increases with the phenyl content of the copolymers except for copolymer C which has a higher stability than might be expected. Comparison with their end-blocked analogues (Figure 4.4 (ii)) shows that the end-blocked samples are more stable. This is the reverse of the evidence of TGA (except for copolymers A and B).

(ii) Analysis of products

a) Benzene evolution

The amounts of benzene produced by the copolymers at 300°C and 500°C are shown on Table 4.3.

As with the results from polymethylphenyl siloxanes, the end-blocked copolymers produce no benzene at 300°C but evolve more benzene than their equivalent hydroxy ended copolymers at 500°C. The amounts of benzene from the end-blocked copolymers increase with % phenyl content.

Qualitative Analysis

NMR was of little use due to the complexity of the mixture of degradation products.

GLC conditions were established for the separation of possible degradation products (Figure 4.5). The majority

FIGURE 4.4 (i)

% Weight Loss vs Time for Dimethyl/methylphenyl Copolymers

(Hydroxy Ended) at 500°C

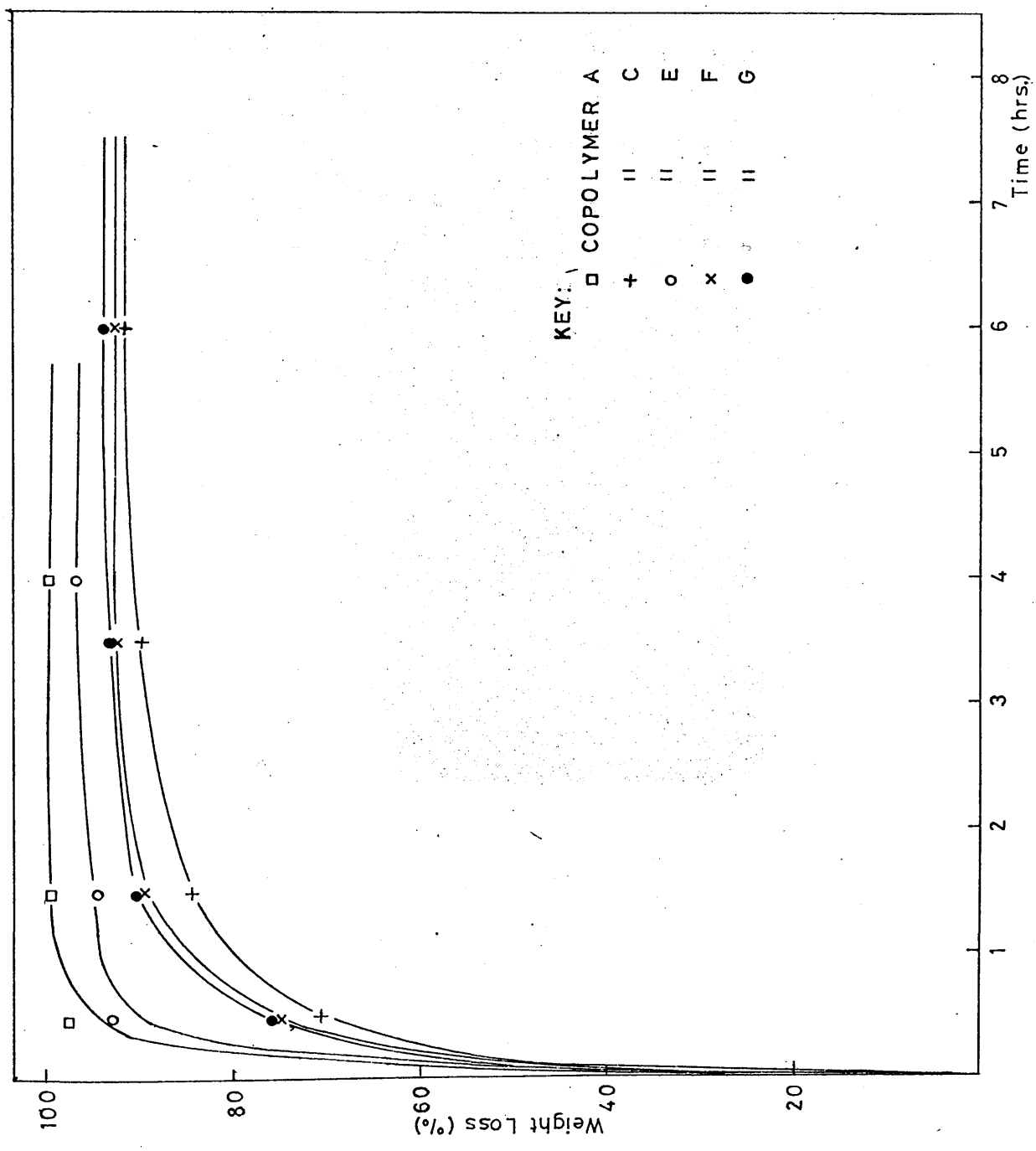


FIGURE 4.4 (ii)

% Weight Loss vs Time for Dimethyl/methylphenyl Copolymers

(Hydroxy Ended and End-blocked) at 500°C

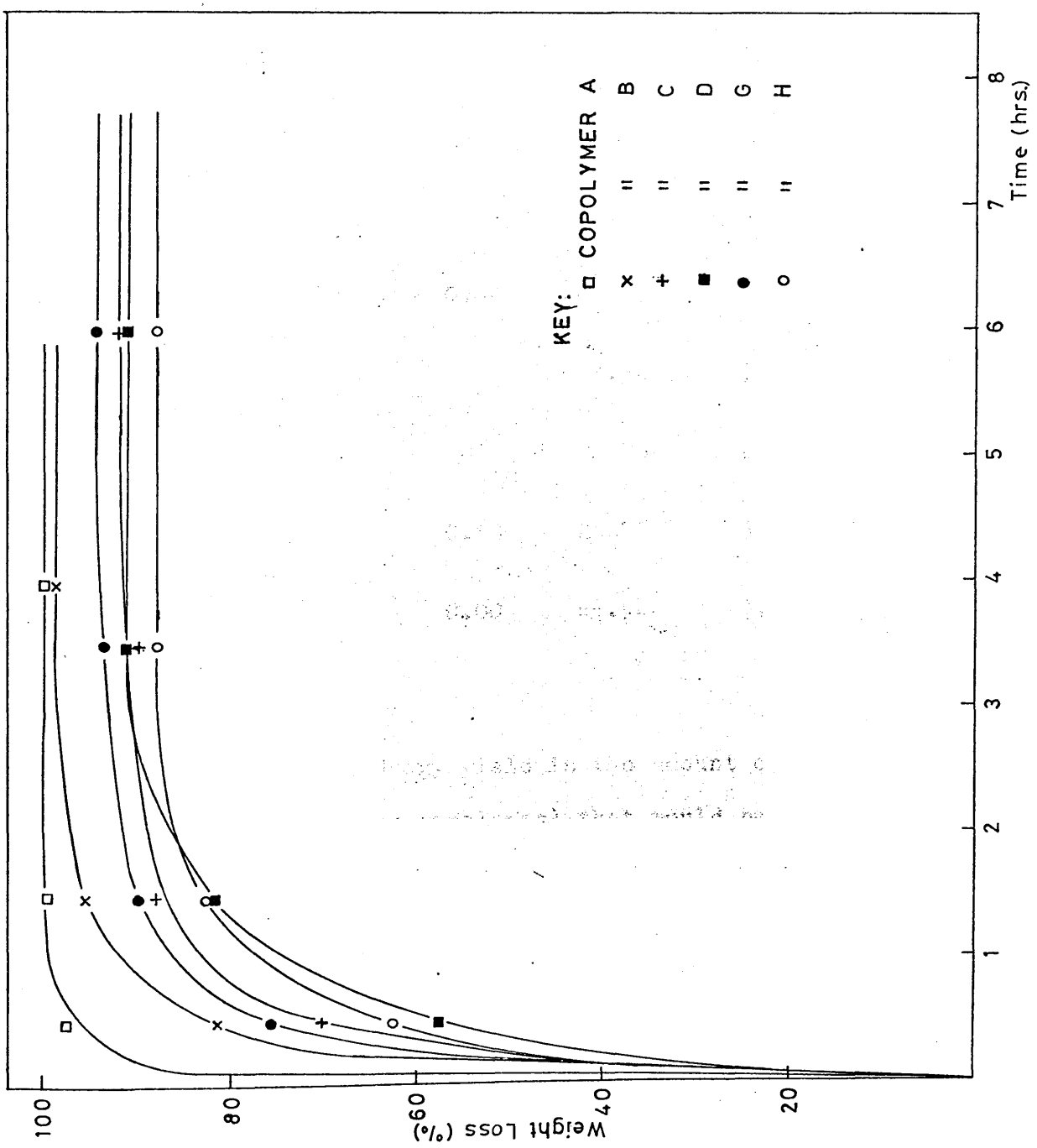


TABLE 4.3

Benzene Evolution from Dimethyl/methylphenyl Copolymers

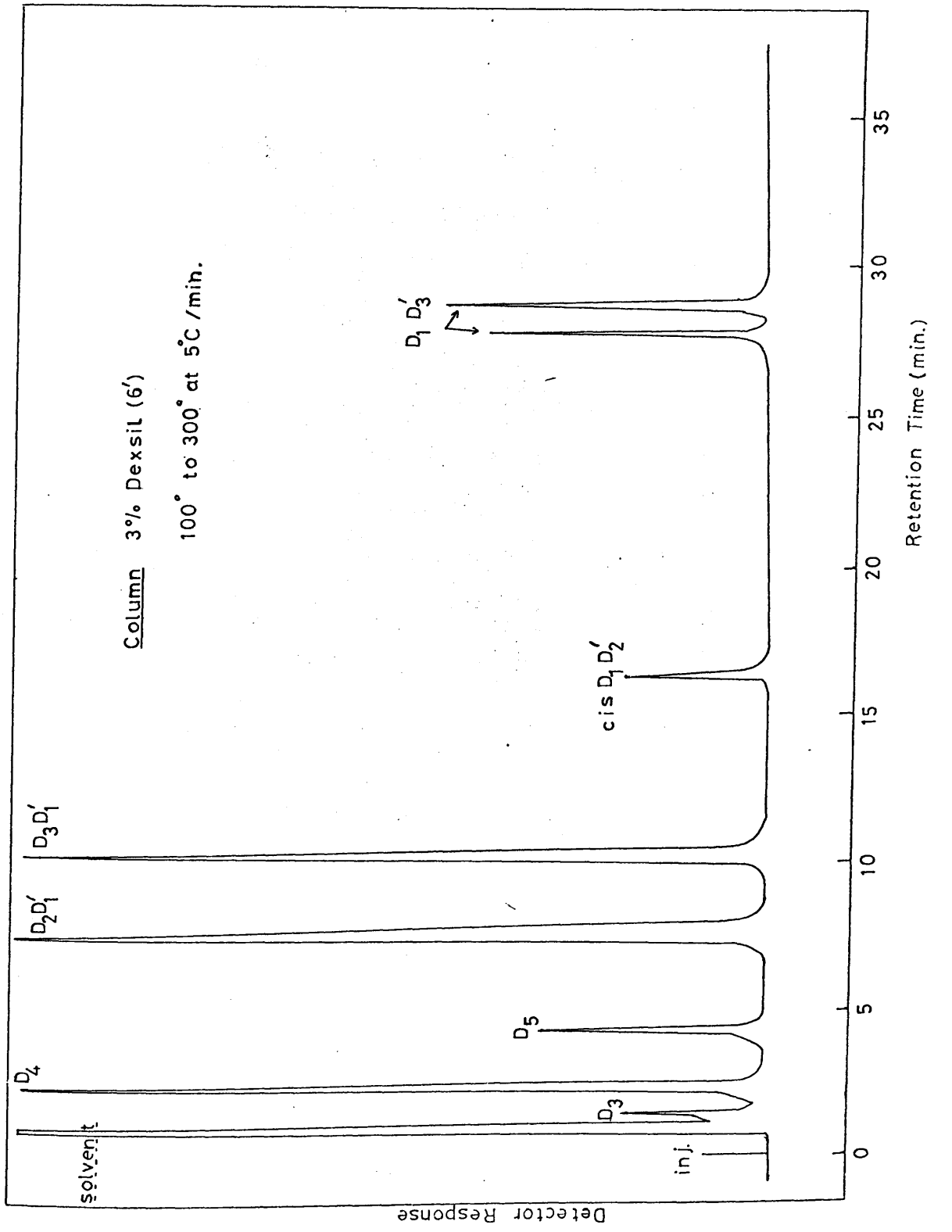
(Moles x 10^{-5}/g. of copolymer)

Copolymer	% Phenyl Content	300°C	500°C	Theoretical* Hydroxy Yield
A	6.25	-	0.43	0.84
B	6.25	-	1.02	0.00
C	12.50	0.01	2.71	0.75
D	12.50	0.00	3.85	0.00
E	16.67	-	3.32	3.12
F	33.37	-	26.75	1.30
G	37.33	0.58	28.89	3.97
H	37.33	0.00	44.94	0.00

* The theoretical hydroxy yield is the amount of benzene (in moles x 10^{-5}/g. of copolymer) that would be produced if every hydroxy chain end reacted to give 1 molecule of benzene.

FIGURE 4.5

GLC Trace of Possible Degradation Products of Polydimethyl/methylphenyl Siloxane



of the degradation products could only be identified by GCMS.

The GCMS trace of a mixture of degradation products from copolymers C and G (at 500°C) is shown on Figure 4.6, and the m/e values for the parent ions for the compounds, along with their proposed structure, are given on Table 4.4.

It is proposed that peaks 1, 3, 5, 14, 17, 18 and 27 are due to bicyclic compounds of a similar nature to those described in Chapter 3. The structures suggested for these compounds are shown in Table 4.5.

Quantitative Analysis

Quantitative analysis of the cyclic degradation products was carried out as described in Chapter 2. The amounts of each compound (expressed as % weight) along with their Rf values are shown on Table 4.6. The compounds were identified by their retention times (under similar conditions to the GCMS run) and by injecting mixtures containing extra amounts of positively identified cyclics.

For a clearer insight into the trends in the degradation of these copolymers, Table 4.7 compares relative amounts of pure dimethyl cyclics produced, with the amounts of pure methylphenyl cyclics and dimethyl/methylphenyl 'mixed' cyclics.

At 500°C, the amounts of dimethyl cyclics decrease with increasing methylphenyl content of the copolymer, whereas the amounts of methylphenyl cyclics increase.

The relative amounts of mixed cyclics produced at 500°C are higher than at 300°C.

FIGURE 4.6

GCMS Trace of Degradation Products from Polydimethyl/
/methylphenyl Siloxanes

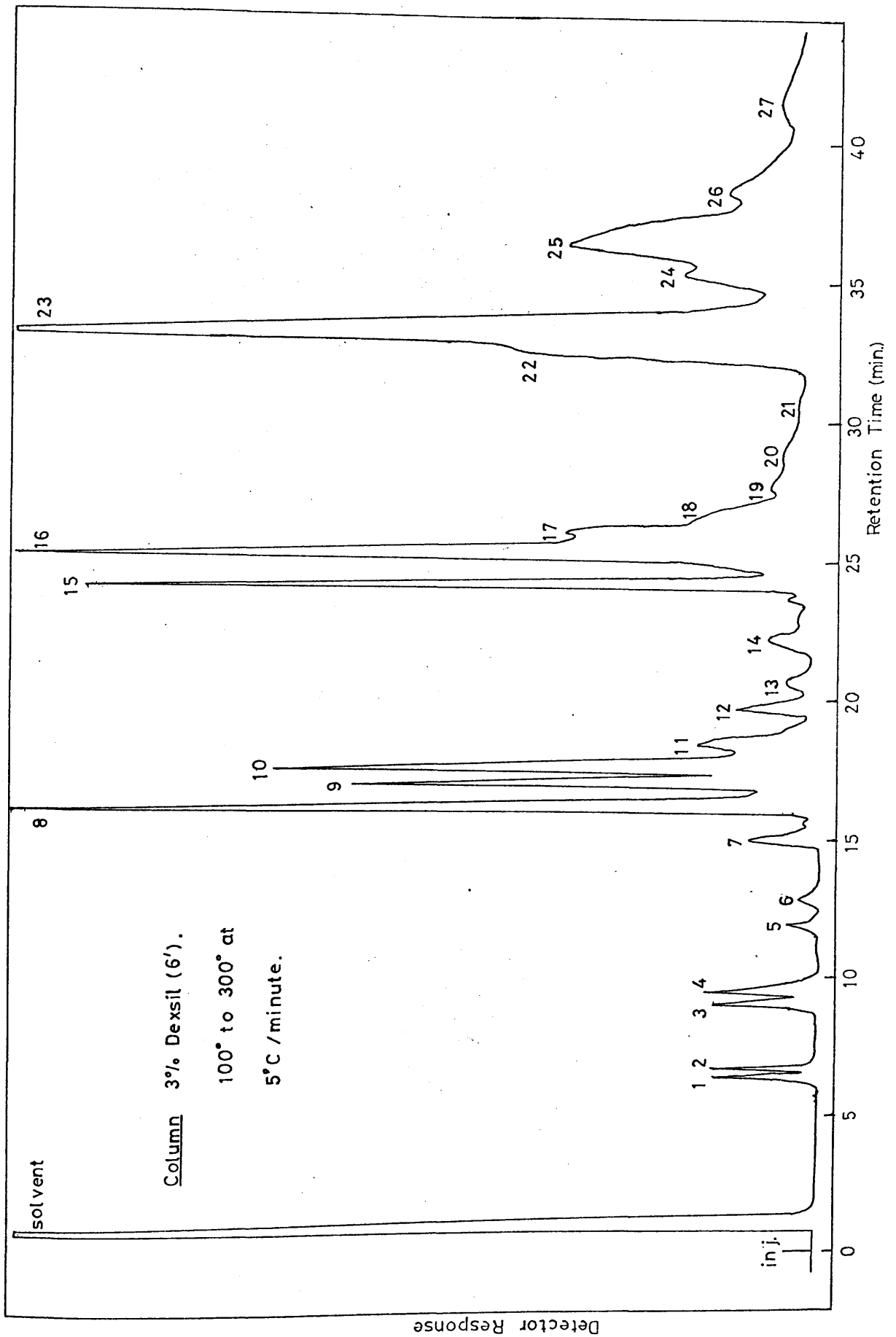


TABLE 4.4

GCMS Analysis of Degradation Products from Polydimethyl/ /methylphenyl Siloxane

Peak	Retention Time (Minutes)	m/e of Parent Ion	Proposed Structure
1	6.41	265 (M-15)+	*
2	6.70	355 (M-15)+	D_5
3	8.94	339 (M-15)+	*
4	9.32	284 M+	D_2D_1'
5	11.92	413 (M-15)+	*
6	12.84	280 (M-78)+	D_3D_1'
7	15.01	354 (M-78)+	D_4D_1'
8	16.27	346 M+	cis D_1D_2'
9	16.91	346 M+	trans D_1D_2'
10	17.08	420 M+	D_2D_2' isomers
11	18.49	420 M+	
12	19.72	479 (M-15)+	D_3D_2' isomers
13	20.66	479 (M-15)+	
14	22.23	400 (M-78)+	*
15	24.08	408 M+	cis D_3'
16	25.33	408 M+	trans D_3'
17	26.10	466 M+	*
18	27.05	466 M+	*
19	27.67	467 (M-15)+	D_1D_3'
20	29.41	541 (M-15)+	D_2D_3' isomers
21	30.67	541 (M-15)+	
22	31.71	544 M+	D_4' isomers
23	33.33	544 M+	
24	35.34	544 M+	
25	36.41	No mass spec obtained	D_1D_4' isomers
26	38.30	618 M+	
27	41.27	602 M+	*

*See Table 4.5 for proposed structures

TABLE 4.5 (i)

Proposed Structure of Bicyclic Compounds from Degradation of Polydimethyl/methylphenyl Siloxanes

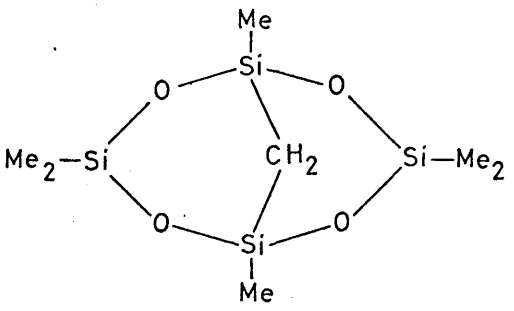
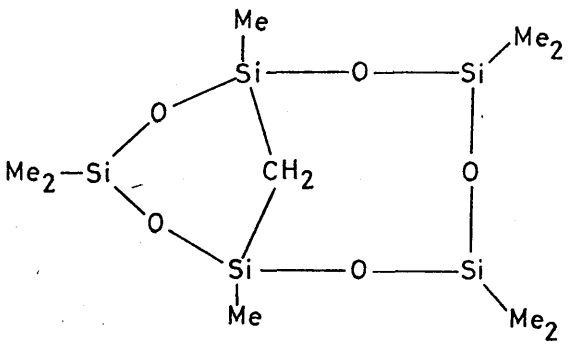
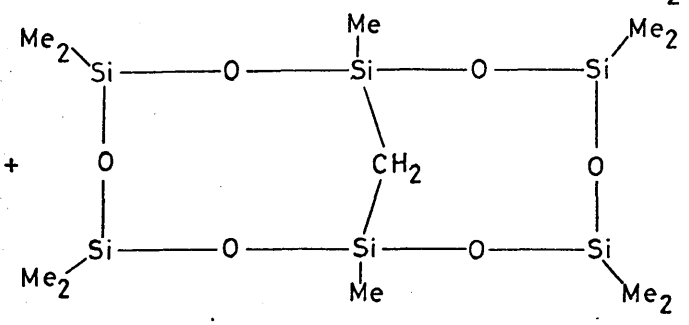
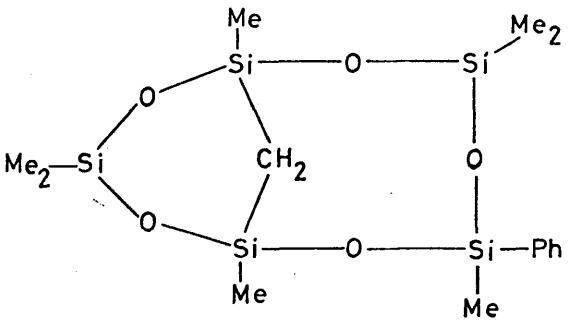
Peak	m/e of Parent Ion	Proposed Structure
1	265 (M-15)+	
3	339 (M-15)+	
5	413 (M-15)+	
14	400 (M-78)+	

TABLE 4.5 (ii)

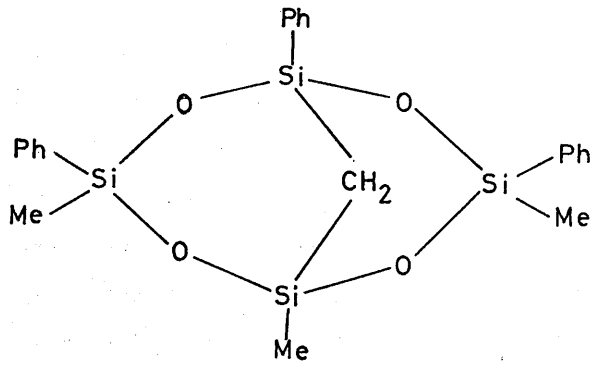
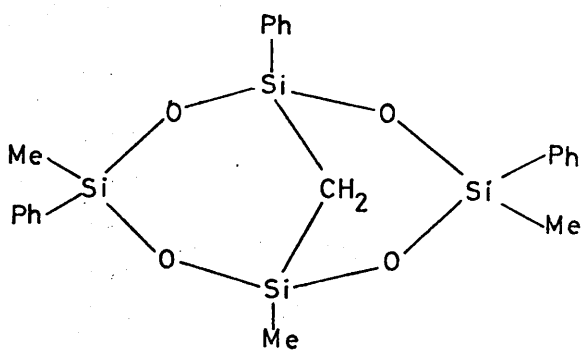
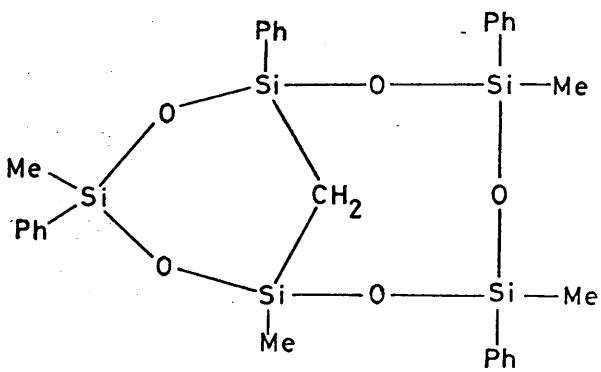
Peak	m/e of Parent Ion	Proposed Structure
17	466(M)+	
18	466(M)+	
27	602(M)+	

TABLE 4.6 (i)

Degradation Products (% Weight) at 500°C from Polydimethyl/methylphenyl Siloxanes

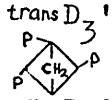
Compound	Rf Value (*Est.)	A	B	C	D	E	F	G	H
D_3	0.88	8.3	6.6	1.6	2.1	2.5	0.0	0.0	0.0
D_4	0.94	4.0	3.5	<1.0	1.1	1.3	0.0	0.0	0.0
	0.92*	0.0	0.0	<1.0	0.0	0.0	0.0	0.0	0.0
D_5	0.94	1.8	1.4	<1.0	1.0	<1.0	0.0	0.0	0.0
	0.95*	0.0	0.0	<1.0	0.0	0.0	0.0	0.0	0.0
D_6	0.96*	7.2	2.7	1.1	1.0	0.0	<1.0	<1.0	0.0
D_2D_1'	1.00	25.5	56.1	25.4	47.6	35.4	1.1	5.8	10.0
	0.95*	0.0	<1.0	1.0	0.0	0.0	0.0	0.0	0.0
D_3D_1'	1.02	9.2	16.5	9.6	11.3	6.4	<1.0	<1.0	1.4
?	1.02*	<1.0	3.7	1.0	0.0	0.0	0.0	0.0	0.0
?	1.02*	1.5	2.3	2.0	1.2	<1.0	<1.0	0.0	0.0
D_4D_1'	1.03	5.4	<1.0	2.4	<1.0	<1.0	<1.0	0.0	0.0
cis D_1D_2'	1.04	1.8	2.3	11.8	5.7	13.1	9.3	8.3	10.7
trans D_1D_2'	1.04	2.1	1.3	16.5	5.2	13.1	8.5	10.3	9.7
D_2D_2'	1.05*	11.2	<1.0	8.5	6.6	12.5	6.9	5.0	3.7
D_3D_2'	1.06*	4.3	0.0	2.6	2.7	1.6	2.4	<1.0	<1.0
D_4D_2'	1.06*	7.0	0.0	2.9	2.8	0.0	1.3	0.0	2.1
cis D_3'	1.07	<1.0	<1.0	1.1	1.6	1.9	6.2	12.9	9.5
trans D_3'	1.07	2.1	<1.0	5.3	6.2	7.3	24.5	39.0	32.9
	1.09*	0.0	0.0	0.0	0.0	0.0	0.0	<1.0	<1.0
D_1D_3'	1.09*	3.7	1.9	2.0	2.3	2.6	15.0	9.6	8.2
D_2D_3'	1.10*	1.0	0.0	<1.0	1.1	<1.0	4.9	<1.0	1.3
D_3D_3'	1.10*	1.3	0.0	1.2	<1.0	0.0	1.9	0.0	0.0
D_4'	1.11	1.6	0.0	<1.0	1.2	0.0	13.9	5.8	7.8
D_1D_4'	1.12*	0.0	0.0	0.0	0.0	0.0	2.3	0.0	0.0
D_5'	1.14*	0.0	0.0	0.0	0.0	0.0	1.5	1.4	2.3

TABLE 4.6 (ii)

Degradation Products (% Weight) at 300°C from Polydimethyl/methylphenyl Siloxanes

Compound	Rf Value (*Est.)	C	D	G	H
D_3	0.88	8.9	12.4	0.0	0.0
C	0.90*	2.4	5.1	0.0	0.0
D_4	0.94	7.2	10.9	0.0	0.0
D_2D_1'	1.00	0.0	<1.0	0.0	0.0
cis D_1D_2'	1.04	4.2	3.5	10.5	13.8
trans D_1D_2'	1.04	10.6	7.9	9.9	13.8
D_2D_2'	1.05*	23.2	10.4	2.4	3.7
D_3D_2'	1.06*	1.0	6.0	<1.0	<1.0
D_4D_2'	1.06*	1.0	<1.0	0.0	0.0
cis D_3'	1.07	5.2	5.1	13.1	10.7
trans D_3'	1.07	11.4	13.6	50.7	37.2
D_1D_3'	1.09*	0.0	0.0	6.9	7.3
D_2D_3'	1.10*	0.0	0.0	<1.0	1.3
D_3D_3'	1.10*	0.0	0.0	<1.0	<1.0
D_4'	1.11	11.0	8.2	5.5	9.6
D_1D_4'	1.12*	13.8	15.4	0.0	0.0
D_5'	1.14*	0.0	0.0	<1.0	<1.0

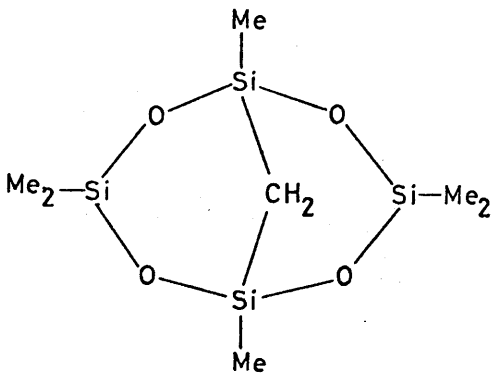
TABLE 4.7

Relative Amounts of Cyclic Degradation Products from Polydimethyl/methylphenyl Siloxanes

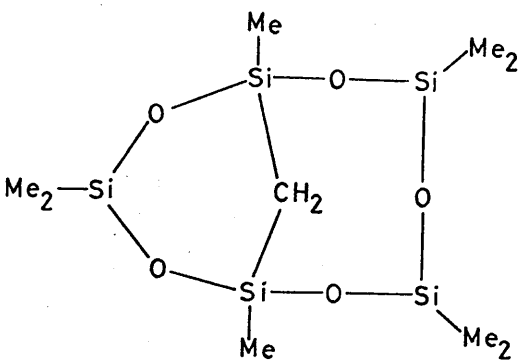
Copolymer	Total % Weight of Dimethyl Cyclics		Total % Weight of Mixed Cyclics		Total % Weight of Methylphenyl Cyclics	
	300°C	500°C	300°C	500°C	300°C	500°C
A	-	21.3	-	74.5	-	4.2
B	-	14.7	-	84.9	-	1.0
C	18.5	5.7	53.9	87.4	27.6	6.9
D	28.4	4.7	44.7	86.1	26.9	9.2
E	-	4.3	-	86.5	-	9.2
F	-	0.0	-	55.4	-	44.6
G	0.0	0.0	30.2	32.3	69.8	57.7
H	0.0	0.0	42.0	49.8	58.0	50.2

4.7 Discussion

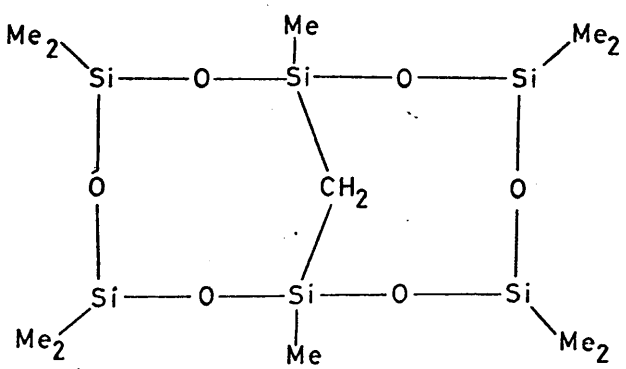
As with polymethylphenyl siloxanes, polydimethyl/ /methylphenyl siloxanes degrade to give benzene and siloxane ring compounds. The amounts of benzene at 300°C are consistent with the hydroxy end group mechanism described in Chapter 3, and again at 500°C, there is evidence of the production of bicyclic compounds as from polymethylphenyl siloxane. Of the bicyclic compounds identified, three must contain a methylene bridge i.e.



GCMS Peak 1



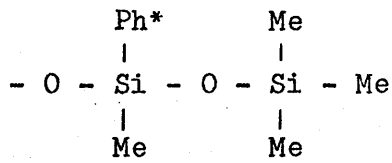
Peak 3



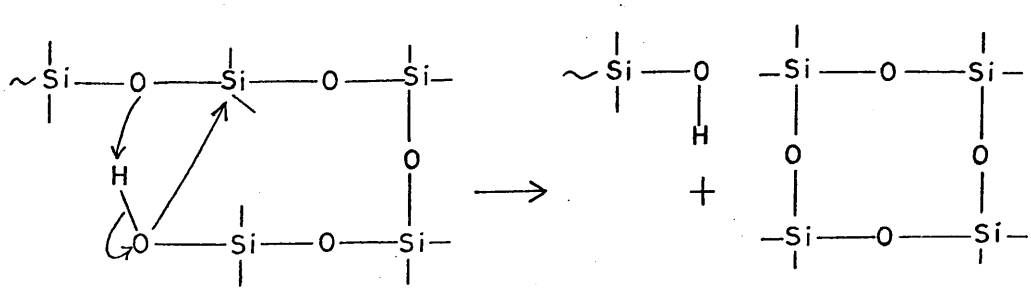
Peak 5

The three other bicyclics could have either a methylene or a phenylene bridge.

At 500°C, the end-blocked samples give higher amounts of benzene than the hydroxy ended ones and have larger residues. It is thought that end-blocking produces labile phenyl groups* - due to an unsymmetrical electronic environment - similar to polymethylphenyl siloxane i.e.



Under TGA conditions copolymers A and B (with a very low methylphenyl:dimethyl ratio) behave similarly to polydimethyl siloxane i.e. end-blocking the polymer reduces the rate of degradation since the hydroxyl group is involved in depolymerisation by the following mechanism:



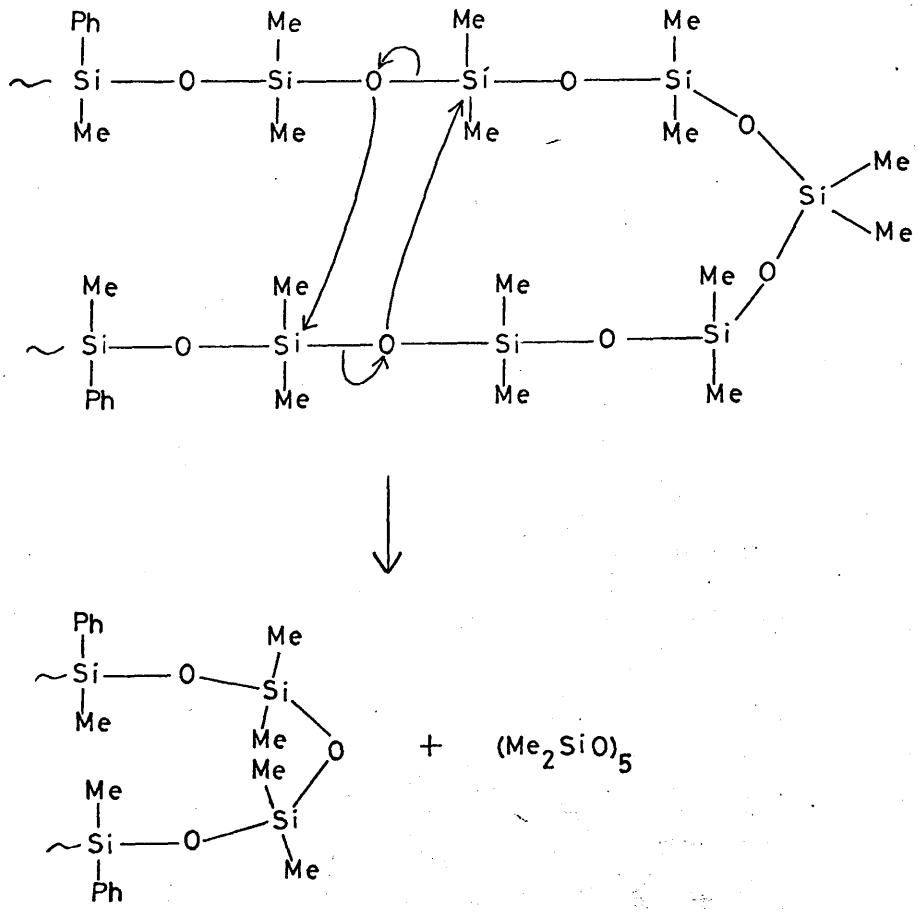
With higher methylphenyl:dimethyl ratios, the hydroxy ended copolymers are more stable than the end-blocked ones since the hydroxy end group is involved in the stabilisation reaction described in Chapter 3.

Under the programmed heating conditions used for TGA ($10^{o}C$/min) depolymerisation will occur more readily at lower temperatures from the end-blocked samples since they cannot form cross-links via the hydroxy chain end mechanism. As the temperature rises further, the second mechanism for benzene evolution - as described in section 3.7 - will come into play and will slow down depolymerisation reactions from both the end-blocked and hydroxy ended copolymers because the increasing number of cross-links will lower the mobility of the chains. Under isothermal conditions ($500^{o}C$), the second mechanism will become important much earlier in the degradation so preventing the end-blocked copolymers from depolymerising faster than the hydroxy ended ones. Since the former samples produce more benzene at $500^{o}C$ - and therefore more cross-links - they will have larger residues.

At first sight it is difficult to envisage a mechanism to account for the formation of cyclics containing only methylphenyl units from copolymers A and B - and to a lesser extent from copolymers C, D, E and F - because of the low methylphenyl:dimethyl ratio. If the methylphenyl units are randomly distributed in A and B, sequences of seven dimethyl siloxane units, on average, might be

expected. It has has been shown (Ref: 36) that electron donating groups - such as methyl groups - attached to the silicon atoms weaken the Si-O bond whereas electron withdrawing groups - such as phenyl groups - strengthen the Si-O bond by drawing the oxygen lone pair electrons into the bond. Thus depolymerisation would occur prefer/ entially in the dimethyl siloxane parts of the chain by random elimination or by intermolecular rearrangements e.g.

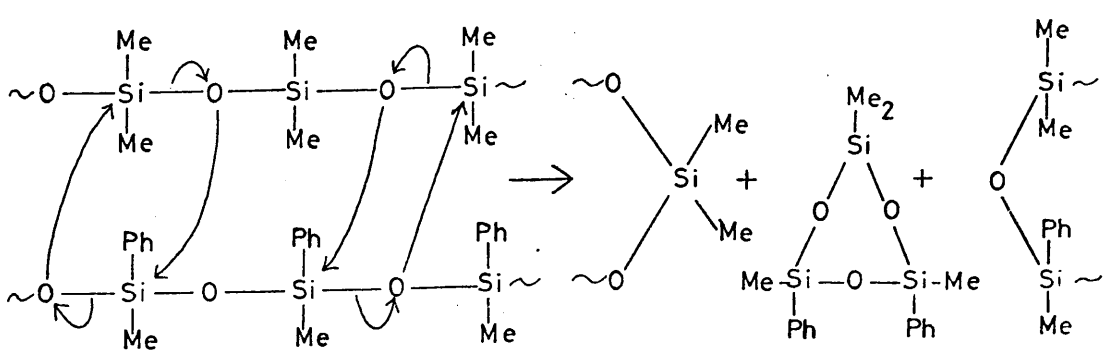
by random elimination


Ph
Me
Si
O
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
Ph
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me
Me

Thus the residue would become progressively poorer in dimethyl units until sections of the chain consisted solely of methylphenyl units which could then break down to form methylphenyl cyclics.

At 300°C the amounts of dimethyl cyclics and methyl/phenyl cyclics compared to the amounts of 'mixed' cyclics, are larger than at 500°C. It is proposed that this is due to the cyclics undergoing secondary rearrangements at the higher temperatures, giving a more random mixture of cyclics.

To test the validity of the proposal that intermolecular reactions are important in the degradation of these copolymers two blends of polydimethyl siloxane and polymethylphenyl siloxane (one with hydroxy ended polymers and the other with both polymers end-blocked) were prepared by evaporation of mixed ether solutions of the polymers. These blends were then degraded isothermally at 300°C and 500°C under vacuum and the products were analysed by GLC. Both blends produced large amounts of dimethyl/methylphenyl 'mixed' cyclics at 300°C and 500°C, proving that polysiloxanes readily undergo intermolecular rearrangements of the following type:



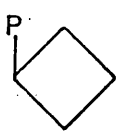
CHAPTER 5

Poly(dimethyldiphenylsiloxane)

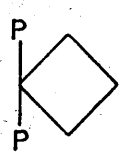
5.1 Introduction

The work described in this Chapter relates to the preparation and thermal decomposition under vacuum of a series of linear polysiloxanes, containing dimethyl and diphenyl units.

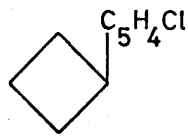
Andrianov and Yakushkina (Ref: 58) in 1958, gave preparative details of three novel siloxane tetramers:



D_3D_1'



D_3D_1''

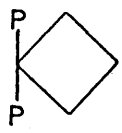


Chlorophenylheptamethyl/ cyclotetrasiloxane

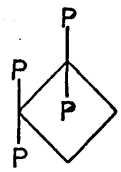
They later (Ref: 64) polymerised these compounds using an acid catalyst at 96°C and found that the rate of polymerisation decreased with the introduction of a

chlorine atom into the phenyl ring and with the number of phenyl groups in the siloxane.

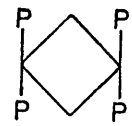
On comparing the rates of anionic polymerisation of cyclics,



A

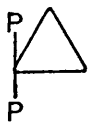


B

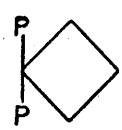


C

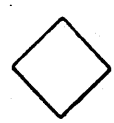
Andrianov et al (Ref: 44) found that compound C had a lower reactivity than A and B which had similar reactivities. They claimed that the difference between B and C was due to the shielding of the phenyl groups in C hindering nucleophilic attack and chain growth. More recently, Andrianov et al (Ref: 65) have compared the reactivity in anionic polymerisations of the following cyclics:



E



F



G

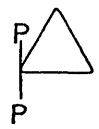
They have demonstrated that both phenyl-containing compounds are more reactive than G due to the electron withdrawing effect of the phenyl groups increasing the ease of nucleophilic attack. They found that the strained six-member ring (compound E) polymerised faster than F which is strain-free.

Laita and Jelinek (Ref: 66) have studied the copoly/merisation of D_4 and D_4'' and claim that the diphenyl tetramer completely polymerises before the dimethyl tetramer. Andrianov et al (Ref: 67) using GPC to analyse the reaction mixture during the early stages of polymer/isation, have demonstrated that dimethyl units are incorporated into the growing polymer early in the reaction, contrary to the observations of Laita and Jelinek. Later work by Andrianov et al (Ref: 68) has shown that in the early stages of the reaction, the copolymer contains a higher percentage of diphenyl units than the starting mixture and that the rate of formation and equilibrium yield of copolymer decreases with increasing initial concentration of diphenyl tetramer.

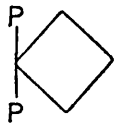
More recently Macfarlane (Ref: 20) has prepared a series of copolymers with up to thirty mole percent diphenyl units by copolymerising dimethyl and diphenyl tetramers. He degraded these polymers under vacuum, and found evidence of Si-C bond cleavage, with the formation of benzene and 'mixed' dimethyl and diphenyl cyclics as degradation products. He also demonstrated that thermal stability increased with the diphenyl content of the copolymers.

5.2 Preparation of Dimethyldiphenyl 'Mixed' Cyclics

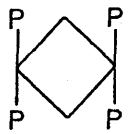
The following dimethyldiphenyl cyclic siloxanes were prepared as described in Chapter 2.



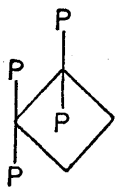
D_2D_1''



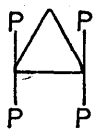
D_3D_1''



D_2D_2''



D_2D_2''



D_1D_2''

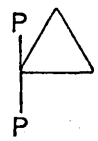
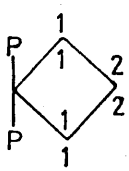
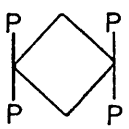
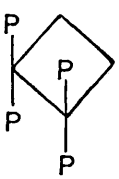
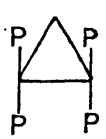
They were characterised by mass spec., NMR, B Pt and M Pt (see Table 5.1 for details) and their purity (> 99.9%) was checked by GLC.

The methyl proton shifts were calculated by the method described by Williams et al (Ref: 50). They have shown that the methyl proton shifts in methylphenyl siloxane ring compounds depend upon the ring size and upon the position and orientation of neighbouring phenyl groups. The values are calculated from the following equation:

$$\gamma = a_0 + a_1x_1 + a_{2c}x_{2c} + a_{2t}x_{2t} + a_{3c}x_{3c} + a_{3t}x_{3t}$$

TABLE 5.1

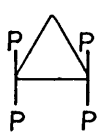
Characterisation of Dimethyldiphenyl 'Mixed' Cyclics

Isomer Structure	Mass Spec (m/e of Parent Ion)	NMR(τ Methyl Protons) Obs.	Calc.*	M Pt (°C) Obs.	Lit.
	346	9.800	9.800	66	65 Ref:65
	420	1)9.882 2)9.938	1)9.879 2)9.927	32	31 Ref:65
	544	9.859	9.854	125	126 Ref:44
	544	9.927	9.902	72	72 Ref:44
	470	9.728	9.722	88	88 Ref:69

*See Table 5.2

where the 'a' values are regression parameters depending on the ring size, and where the 'x' values are structural variables.

The regression parameters (a) for cyclic trimer, tetramer and pentamer siloxanes are reproduced on Table 5.2. The structural variables (x) are specified by the authors as follows; x is unity when the silicon, which bears the observed methyl group also bears a phenyl group, and is zero otherwise; x_{2c} and x_{2t} are the number of adjacent phenyl groups orientated cis and trans respectively to the observed methyl group; x_{3c} and x_{3t} are the number of remote phenyl groups orientated cis and trans, respectively.



Taking dimethyltetraphenylcyclotrisiloxane as an example, the equation becomes:

$$\gamma = 9.878 + (-0.240) \times 0 + (-0.008) \times 2 + (-0.076) \times 2$$

$$\gamma = 9.722$$

Thus there is good agreement between observed and calculated shifts and the structure can be confirmed using other analytical techniques.

TABLE 5.2

NMR Shift-structure Correlations for Methyl Protons in Methylphenyl Siloxane Ring Compounds*

Ring Size	a_0	a_1	a_{2c}	a_{2t}	a_{3c}	a_{3t}
Trimer	9.878	-0.240 ±0.006	-0.001 ±0.004	-0.077 ±0.004	-	-
Tetramer	9.904	-0.224 ±0.005	0.044 ±0.003	-0.069 ±0.003	0.054 ±0.006	-0.031 ±0.006
Pentamer	9.908	-0.277 ±0.010	0.041 ±0.008	-0.056 ±0.008	0.059 ±0.008	-0.008 ±0.008

*Reproduced from Ref: 50

5.3 Preparation of Polydimethyldiphenyl Siloxanes

Six hydroxy ended copolymers with varying dimethyl: diphenyl ratios and two trimethyl silyl end-blocked copolymers were prepared. They were prepared as described in Chapter 2 and Table 5.3 gives details of starting materials, reaction conditions and number average molecular weights of the final copolymers.

5.4 T.G.A.

TGA traces of the hydroxy ended copolymers are shown on Figure 5.1. Figure 5.2 shows the TGA traces of the hydroxy ended copolymers with their end-blocked analogues.

The temperature of initial weight loss and the weight of residue of the hydroxy ended copolymers increases with phenyl content. Copolymer E has a larger residue than copolymer F, although both have the same phenyl content.

End blocking of the copolymers lowers the stability in terms of weight of residue and temperature of initial weight loss.

5.5 T.V.A.

TVA traces for all of the copolymers in the series are shown on Figure 5.3.

The $0^{o}C$ and $-45^{o}C$ piranis on the traces for copolymers A, B, C and D are not coincident with the $-75^{o}C$ and $-100^{o}C$

TABLE 5.3

Preparation of Polydimethyldiphenyl Siloxanes

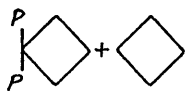
Copolymer	Monomer	Polymerisation Temp (^{o}C)	Catalyst Concn (w/w%)	$\bar{Mn}$	%Phenyl Content
A		120	0.1	1010000	12.5
B		120	0.1	305000	25.0
C	End-blocked sample of Copolymer B			305000	25.0
D		120	0.1	93800	33.3
E		120	0.1	62000	50.0
F		120	0.1	40800	50.0
G		120	0.1	51600	66.7
H	End-blocked sample of Copolymer G			51600	66.7

FIGURE 5.1

TGA Traces of Polydimethyldiphenyl Siloxanes
(Hydroxy Ended Samples)

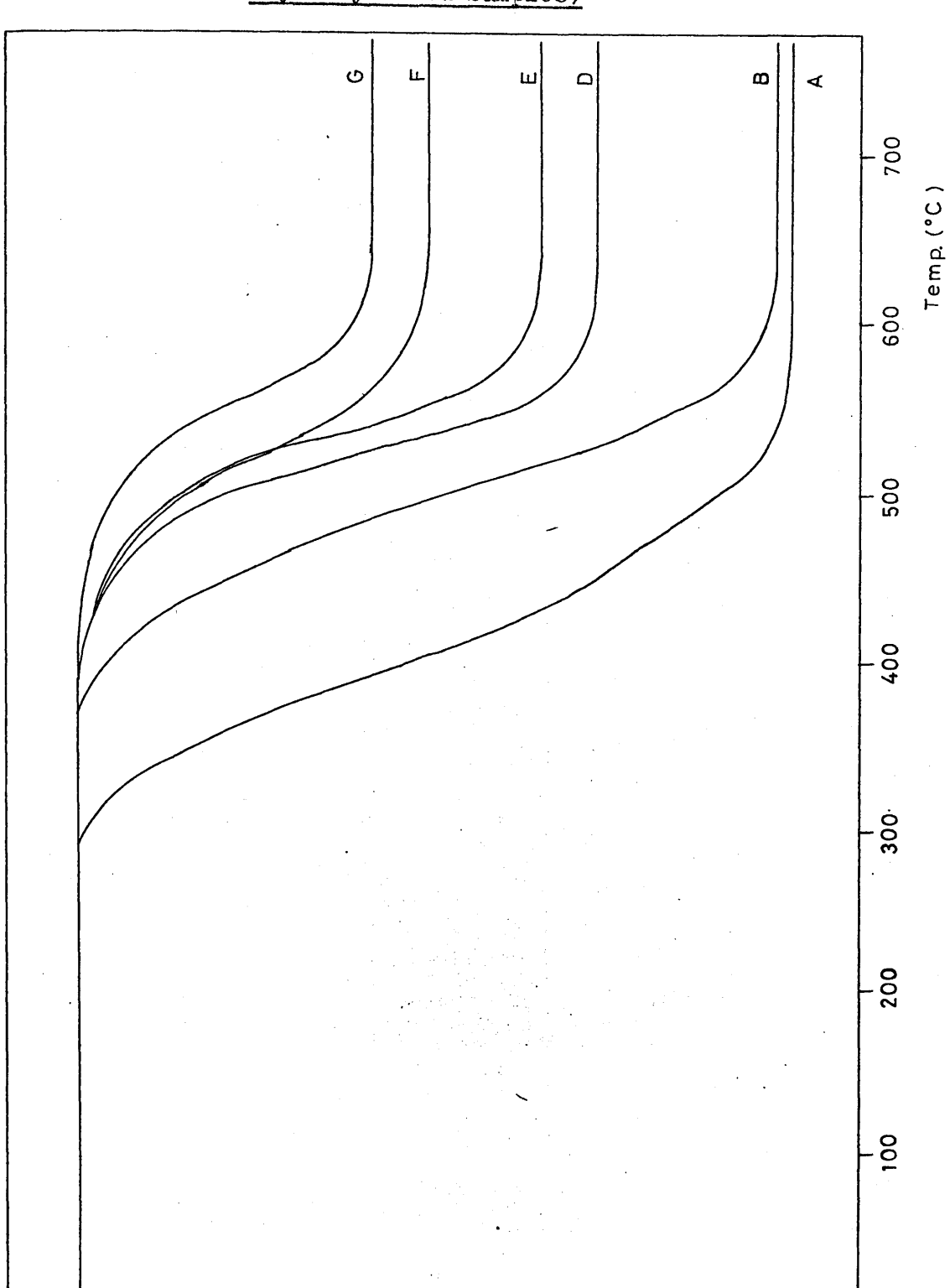


FIGURE 5.2

TGA Traces of Polydimethyldiphenyl Siloxanes
(Hydroxy Ended and End-blocked Samples)

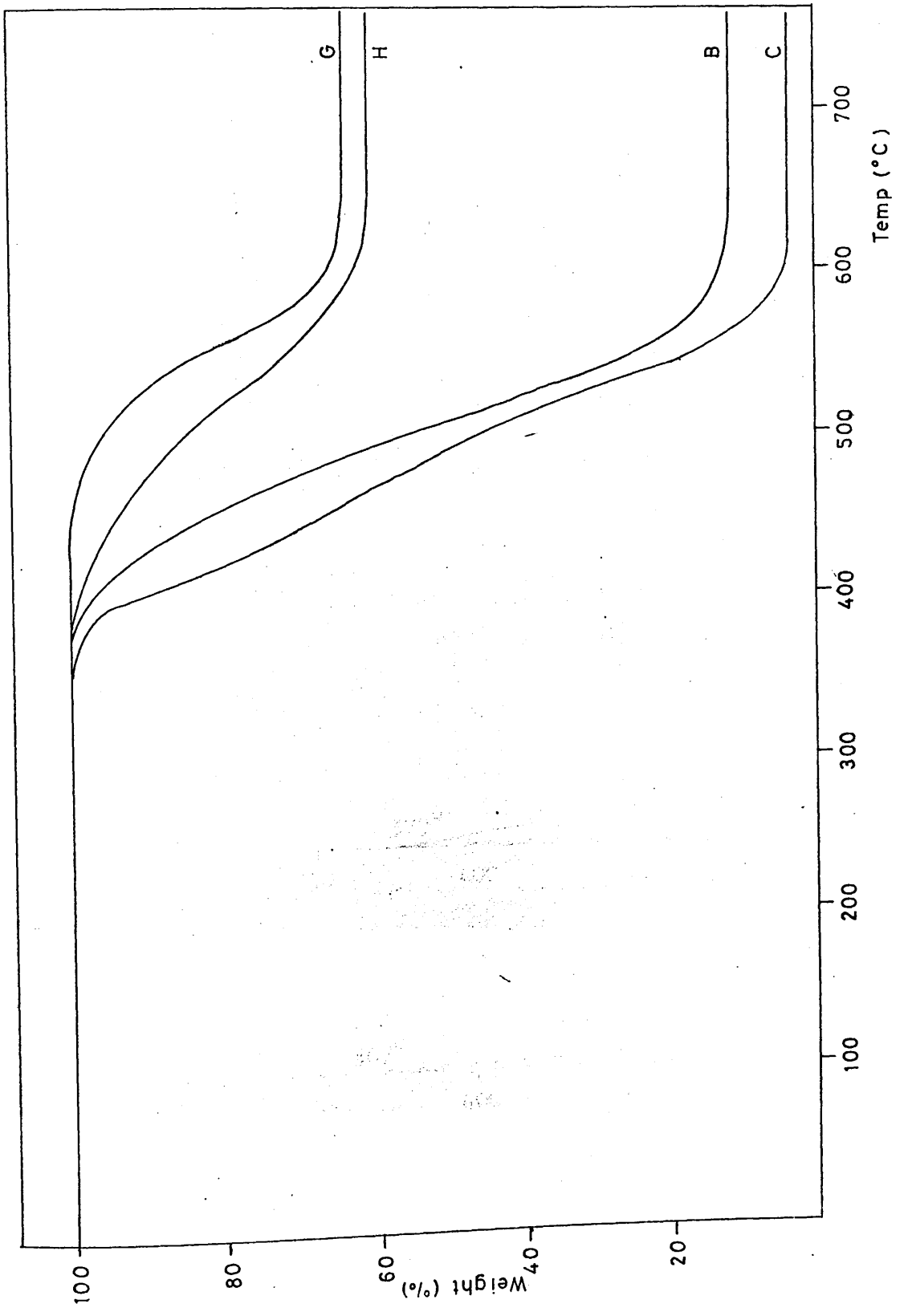


FIGURE 5.3 (i)

TVA Traces of Polydimethyldiphenyl Siloxanes

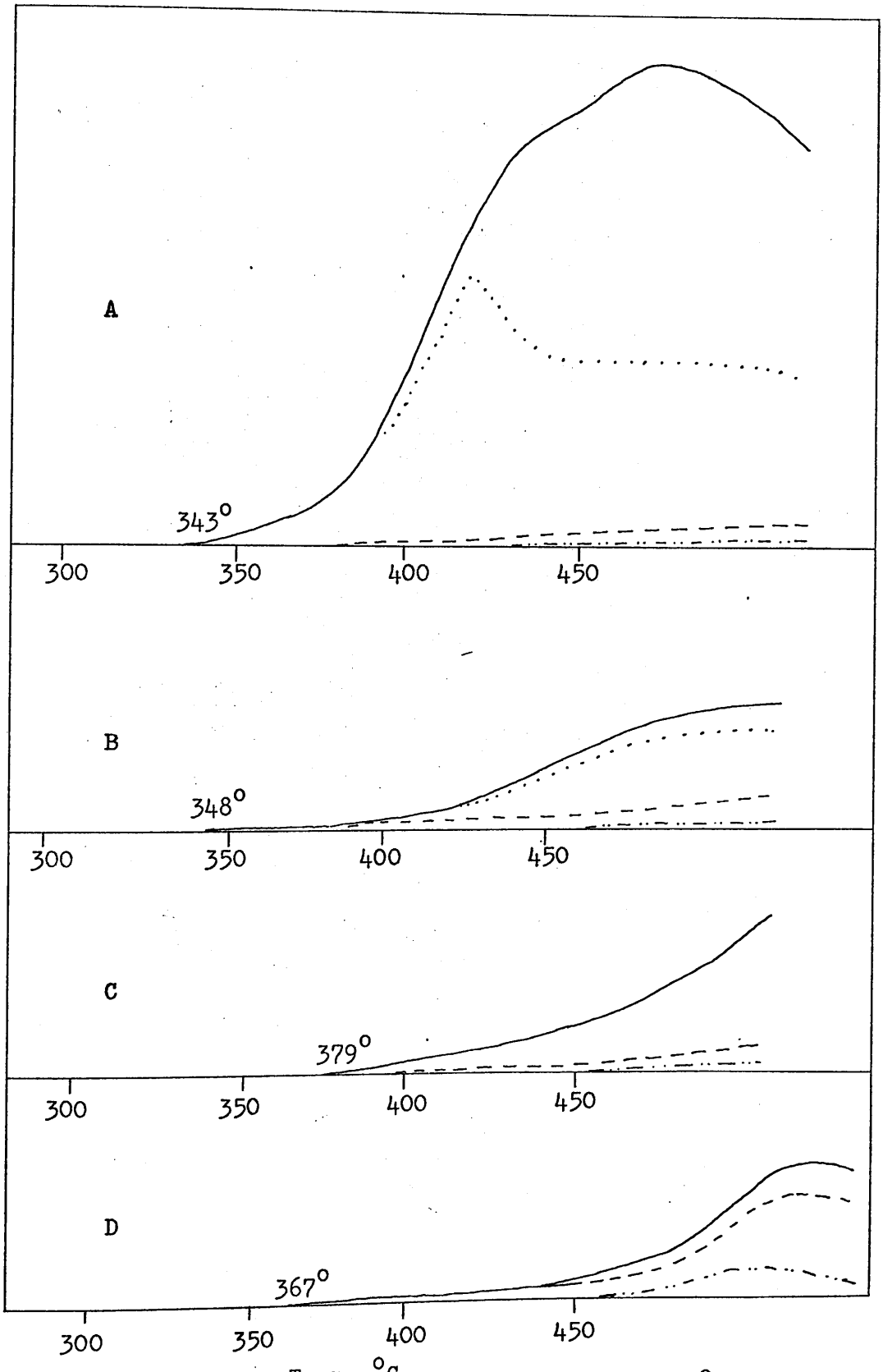
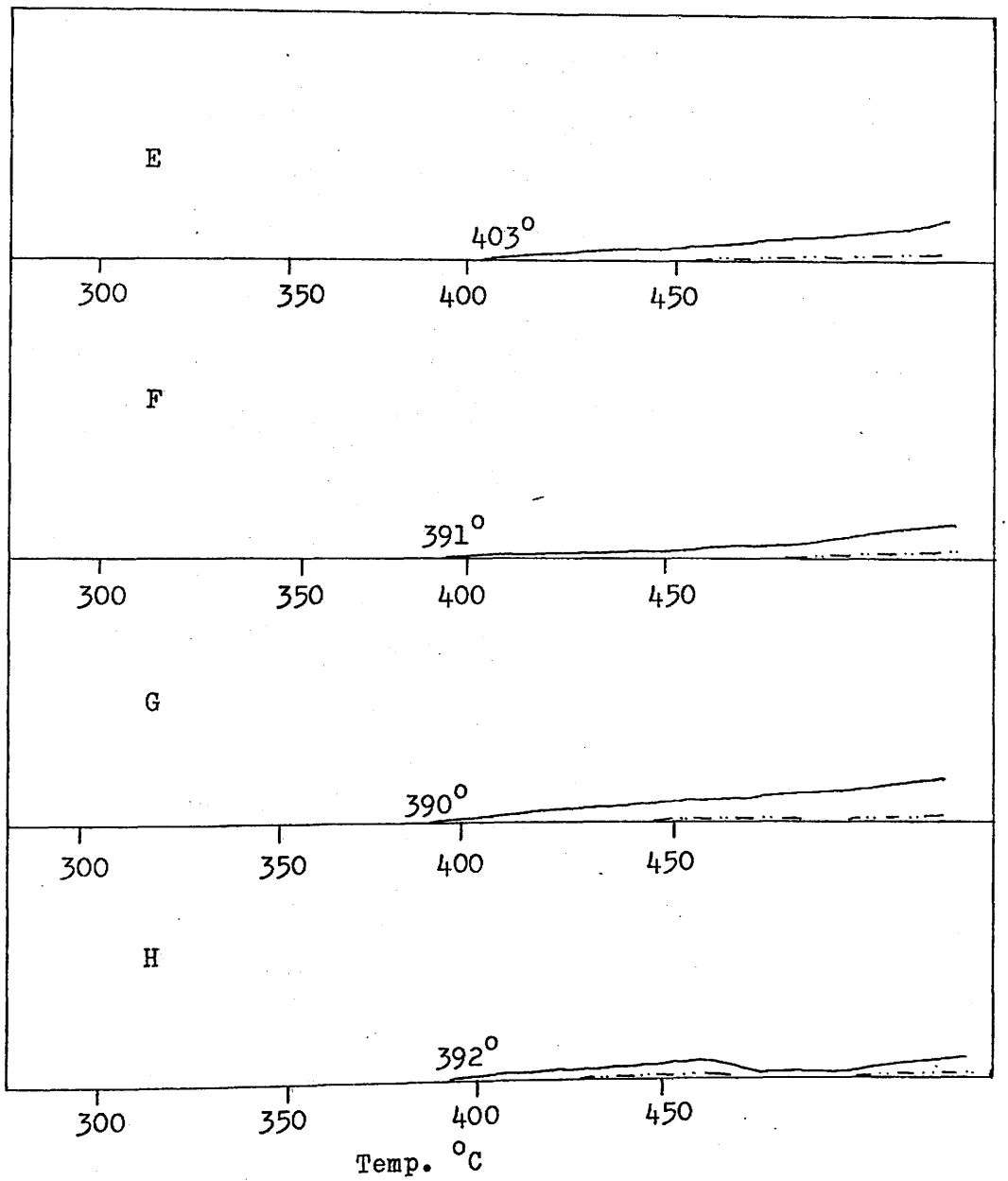


FIGURE 5.3 (ii)

TVA Traces of Polydimethyldiphenyl Siloxanes



piranis - unlike the traces for copolymers E, F, G and H. This is due to the production of dimethyl trimer and tetramer as degradation products - identified by IR - from the former copolymers. The rise in the -75°C and -100°C piranis in all of the traces was due to the evolution of small amounts of benzene. The trace amounts of non-condensables were identified by mass spec as methane from 'closed system' degradations.

Because of the small amounts of volatile products and because the temperature of maximum rate of degradation is greater than 500°C (in most cases) it is difficult to observe any trends in the degradation behaviour of these copolymers. However, it would appear that the temperature of initial degradation of the hydroxy ended copolymers increases with phenyl content and that the end-blocked copolymers start producing volatiles at slightly higher temperatures than their hydroxy ended analogues.

NMR analysis of the 'cold ring' fractions showed them to consist of complex mixtures of dimethyl and dimethyl/diphenyl cyclic siloxanes.

5.6 Vacuum Line Degradation System

This was used to study the evolution of benzene and the distribution of products from the 'cold ring' fraction, from all the copolymers at 500°C and from the hydroxy ended copolymers and their end-blocked analogues at 300°C.

As in previous studies, the first trap at -70°C was used to condense any dimethyl trimer and tetramer formed. These cyclics were then quantitatively combined with the rest of the cyclics from the 'cold ring' fraction.

(i) Isothermal weight loss under vacuum

Figure 5.4 shows the results of weight loss under vacuum at 500°C for all the copolymers.

The salient features from these data are as follows. The stability (as measured by the weight of the residue) of the hydroxy ended copolymers increases with their phenyl content; end-blocked samples are less stable than hydroxy ended ones; copolymer F has a larger residue than copolymer C although both have the same phenyl content (50%). All of these results concur with those from TGA studies.

(ii) Analysis of products

a) Benzene evolution

The amounts of benzene evolved by the copolymers at 300°C and 500°C, after 20 and 10 hours, respectively are shown in Table 5.4.

As with the other systems studied, end-blocked samples do not evolve any benzene at 300°C and the hydroxy ended samples produce slightly less benzene than the 'theoretical hydroxy yield' at 300°C but more than it, at 500°C. The

FIGURE 5.4

% Weight Loss vs Time for Polydimethyldiphenyl Siloxanes at 500°C

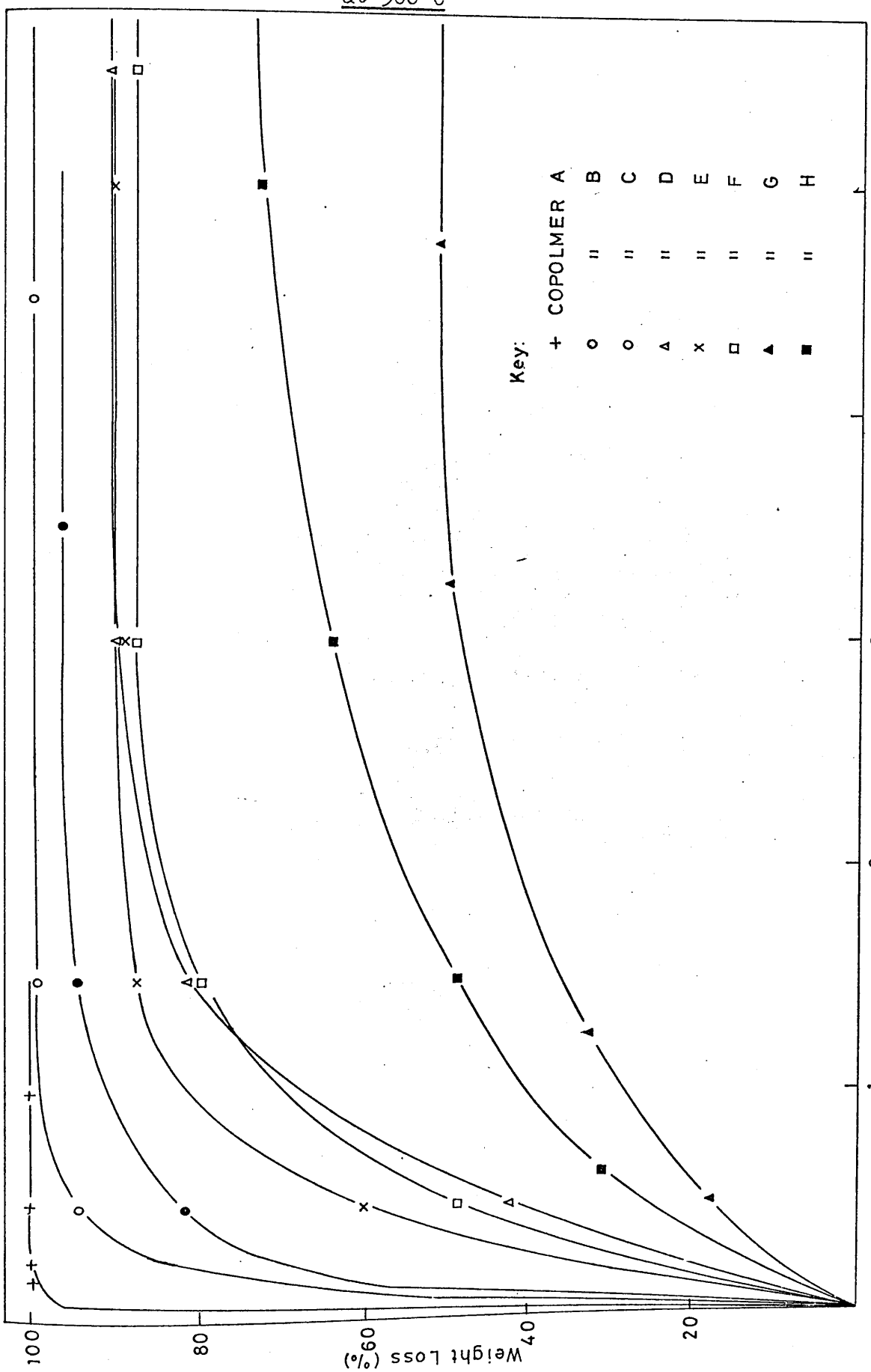


TABLE 5.4

Benzene Evolution from Polydimethyldiphenyl Siloxane Copolymers (Moles x 10^{-5}/g of Copolymer)

Copolymer	%Phenyl Content	300°C	500°C	Theoretical Hydroxy Yield
A	12.5	-	0.32	0.19
B	25.0	0.10	7.60	0.65
C	25.0	0.00	4.28	0.00
D	33.3	-	57.78	2.13
E	50.0	-	85.60	3.22
F	50.0	-	118.77	4.90
G	66.7	0.60	278.20	3.87
H	66.7	0.00	184.04	0.00

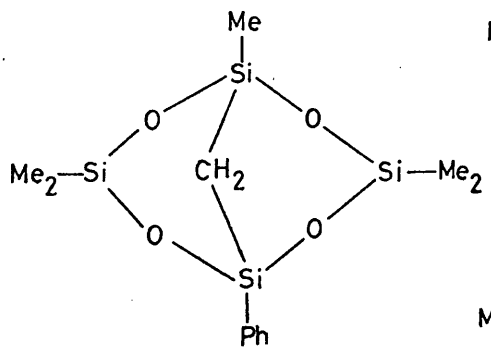
yield of benzene at 500°C increases with the phenyl content of the copolymers - in agreement with the results from the polydimethyl/methylphenyl series. The end-blocked samples, however, evolve less benzene than the hydroxy ended ones - contrary to results from polymethylphenyl and polydimethyl/methylphenyl systems.

b) 'Cold ring' fraction

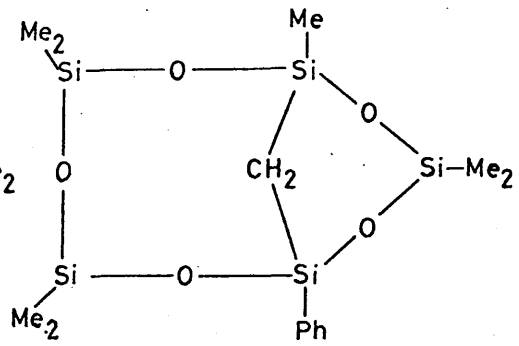
Quantitative analysis

GLC conditions for the separation of possible degradation products were established - a typical trace is shown in Figure 5.5.

GCMS was used to identify those products which could not be synthesised. A GCMS trace of the degradation products of copolymer B (ten hours at 500°C) is shown in Figure 5.6. Table 5.5 gives the m/e values of the parent ions of the compounds along with their proposed structure. Peaks IV and VI are thought to be due to the following bicyclic compounds:



IV



VI

FIGURE 5.5

GLC Trace of Possible Dimethyldiphenyl Siloxane Degradation Products

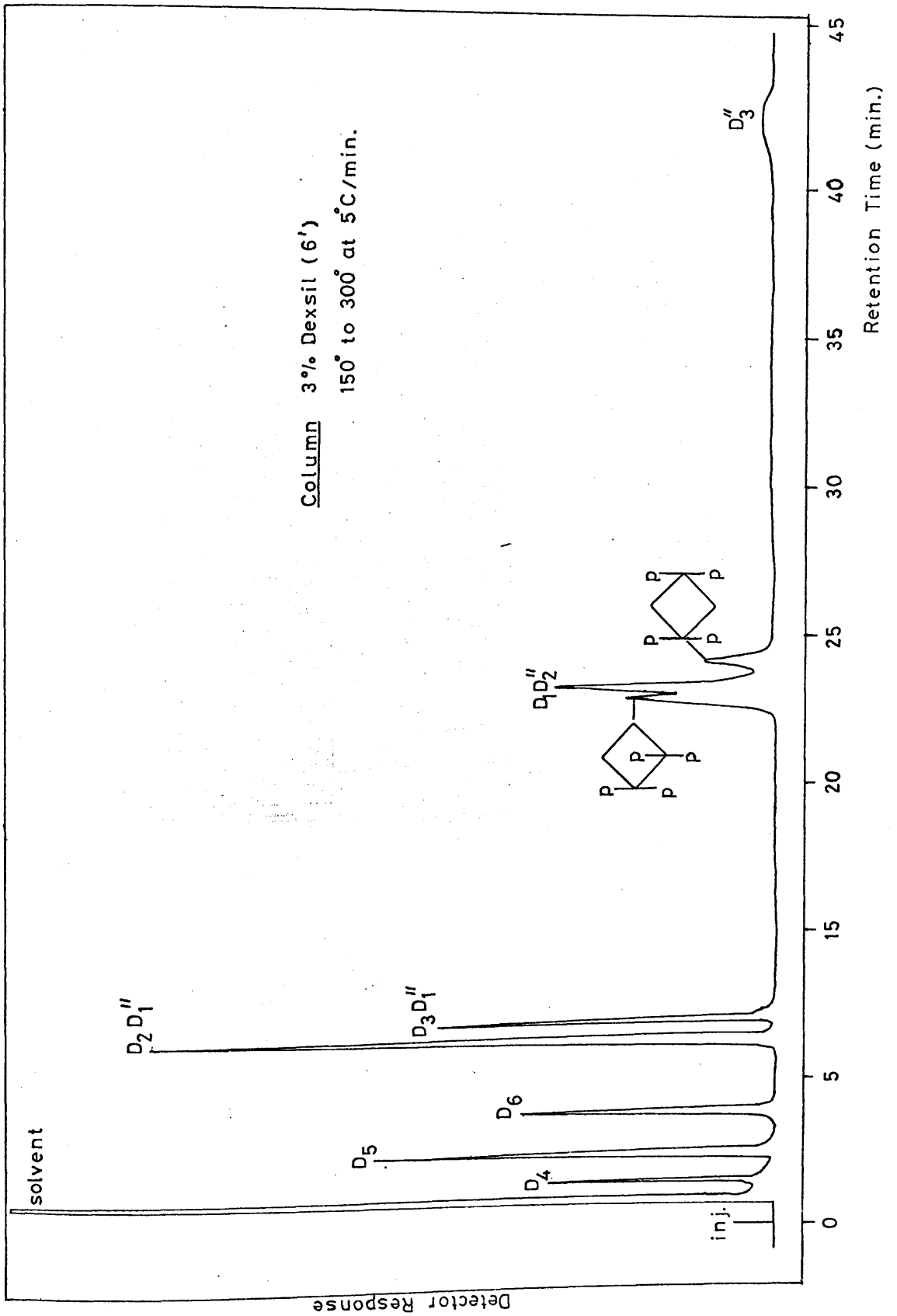


FIGURE 5.6

GCMS Trace of Dimethyldiphenyl Siloxane Degradation Products

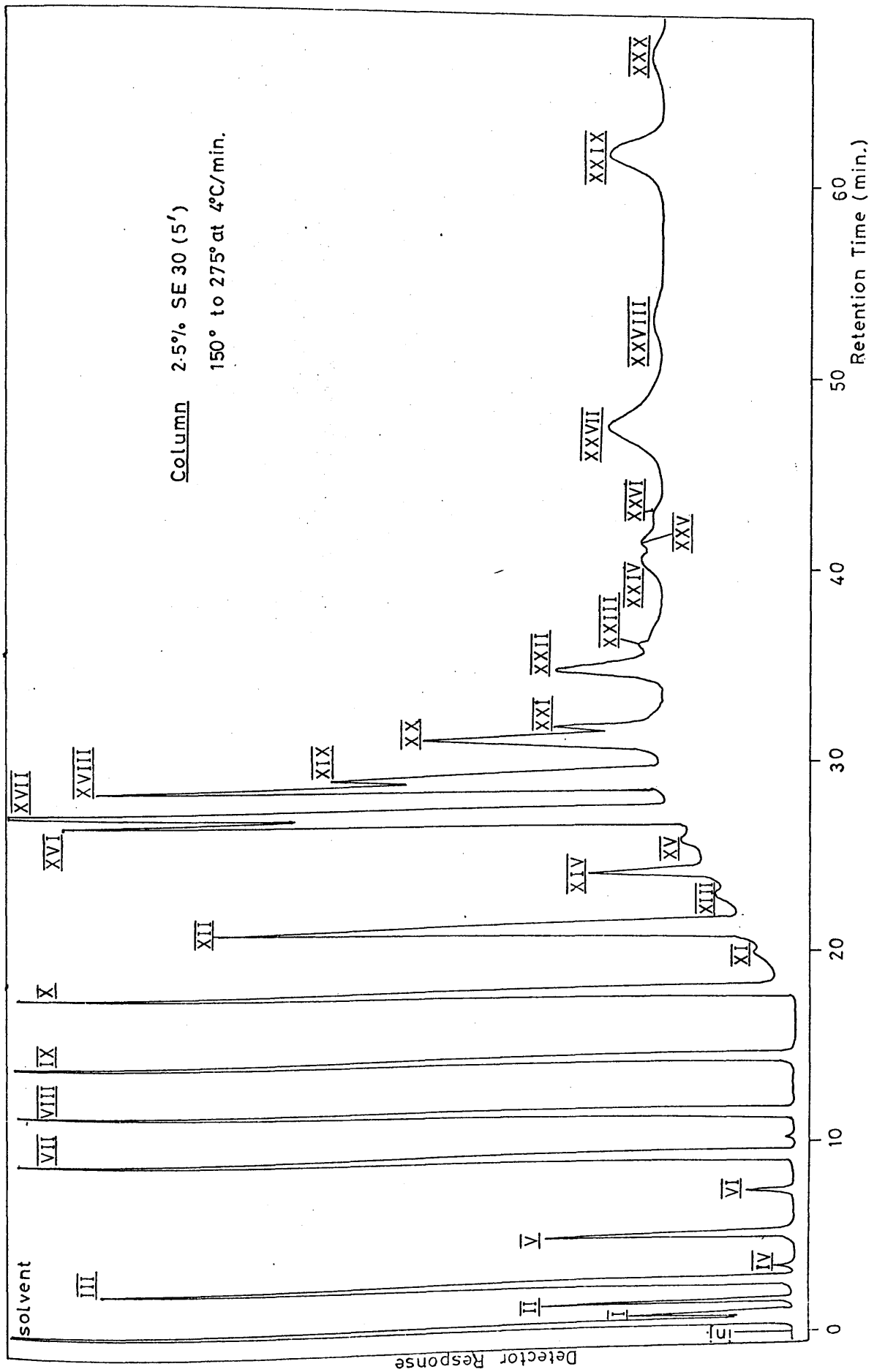


TABLE 5.5

GCMS Analysis of Degradation Products from Polydimethyl/ /diphenyl Siloxanes

Peak	Retention Time (Mins)	m/e (Parent Ion)	Proposed Sructure
I	1.10	281(M-15)+	D_4
II	1.40	355(M-15)+	D_5
III	2.35	429(M-15)+	D_6
IV	3.25	342(M)+	*
V	4.35	503(M-15)+	D_7
VI	7.82	416(M)+	*
VII	9.41	346(M)+	D_2D_1''
VIII	11.83	420(M)+	D_3D_1''
IX	15.20	479(M-15)+	D_4D_1''
X	18.79	553(M-15)+	D_5D_1''
XI	20.68	No mass spec recorded	?
XII	22.05	627(m-15)+	D_6D_1''
XIII	24.39	No mass spec recorded	?
XIV	25.18	701(M-15)+	D_7D_1''
XV	26.99	No mass spec recorded	?
XVI	28.22	544(M)+	cis D_2D_2''
XVII	28.75	470(M)+	D_1D_2''
XVIII	30.06	544(M)+	trans D_2D_2''
XIX	30.55	618(M)+	D_3D_2''
XX	32.60	618(M)+	D_3D_2''
XXI	33.56	692(M)+	D_4D_2''
XXII	36.58	692(M)+	D_4D_2''
XXIII	37.81	No mass spec recorded	D_5D_2''(?)
XXIV	41.90	840(M)+	D_6D_2''
XXV	43.02	No mass spec recorded	D_6D_2''(?)
XXVI	44.59	840(M)+	D_6D_2''
XXVII	49.60	668(M)+	D_1D_3''
XXVIII	55.21	742(M)+	D_2D_3''
XXIX	64.16	No mass spec recorded	D_3''(?)
XXX	68.77	No mass spec recorded	D_2D_3''(?)

*For proposed structure see over

There is no evidence of any bicyclic compounds which contain phenylene bridging groups.

Quantitative analysis

Quantitative analyses of the cyclics produced by these copolymers were carried out using the methods described earlier.

Rf values for compounds which could not be isolated in a pure form were estimated from known Rf values. The compounds were identified by injecting mixtures containing positively identified cyclics and by comparison of retention times from GCMS data. The results for degradations carried out at 500°C and 300°C are shown on Tables 5.6 and 5.7 respectively.

Table 5.8 gives a summary of these results showing the ratios of dimethyl cyclics produced compared to the amounts of dimethyldiphenyl 'mixed' cyclics and diphenyl cyclics(in practice, only D_3'' can be detected by GLC since higher diphenyl cyclics are too involatile).

As might be expected the amounts of dimethyl cyclics produced at 500°C decrease with increasing diphenyl content of the copolymers whereas the diphenyl cyclics produced increase with diphenyl content. Copolymer C produces much greater amounts of dimethyl cyclics at 300°C than its hydroxy ended analogue (copolymerB) but B produces about twice as much dimethyl cyclics as C at 500°C.

TABLE 5.6

Degradation Products (% Weight) at 500°C from Polydimethyl/ /diphenyl Siloxanes

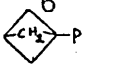
Compound	Rf Value (*Est.)	A	B	C	D	E	F	G	H
D_3	0.86	6.9	3.8	1.9	1.2	0.0	0.0	0.0	0.0
D_4	0.89	3.4	1.9	1.0	<1.0	0.0	0.0	0.0	0.0
D_5	0.91	2.1	1.2	<1.0	<1.0	0.0	0.0	0.0	0.0
D_6	0.92*	4.4	4.9	2.2	<1.0	0.0	0.0	0.0	0.0
	0.92*	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	0.0	0.0
D_7	0.92*	1.3	2.4	1.0	<1.0	0.0	0.0	0.0	0.0
	0.94*	<1.0	<1.0	<1.0	<1.0	0.0	<1.0	0.0	0.0
D_2D_1''	1.00	23.6	33.8	26.0	3.6	20.1	10.8	1.6	25.6
D_3D_1''	1.02	20.5	13.5	11.3	5.9	8.6	4.6	<1.0	2.8
D_4D_1''	1.03*	6.5	3.6	2.6	1.0	1.4	<1.0	0.0	<1.0
D_5D_1''	1.04*	7.5	3.6	1.0	1.9	1.8	<1.0	<1.0	<1.0
?	1.04*	<1.0	0.0	0.0	<1.0	0.0	0.0	0.0	1.1
D_6D_1''	1.04*	2.5	1.4	2.0	<1.0	<1.0	<1.0	<1.0	1.6
?	1.04*	<1.0	<1.0	<1.0	<1.0	2.5	1.3	0.0	<1.0
D_7D_1''	1.04*	<1.0	<1.0	1.4	<1.0	<1.0	<1.0	<1.0	0.0
?	1.08*	<1.0	0.0	<1.0	1.2	<1.0	<1.0	<1.0	0.0
cis D_2D_2''	1.15	3.6	9.7	6.7	14.8	7.9	9.6	3.5	2.6
D_1D_2''	1.11	8.2	13.8	19.9	39.1	30.9	37.6	55.6	29.9
trans D_2D_2''	1.15	3.3	2.9	6.9	8.6	5.5	6.0	2.7	6.6
D_3D_2''	1.17*	3.0	1.3	1.7	2.5	1.2	1.4	1.1	4.9
D_4D_2''	1.19*	<1.0	<1.0	1.6	2.4	<1.0	1.8	<1.0	1.5
D_5D_2''	1.19*	0.0	0.0	<1.0	1.5	<1.0	<1.0	<1.0	1.8
D_6D_2''	1.19*	0.0	0.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
D_1D_3''	1.23*	<1.0	<1.0	<1.0	1.1	1.0	1.7	2.2	1.6
D_2D_3''	1.23*	<1.0	<1.0	3.9	4.7	7.6	11.2	9.9	6.8
D_3''	1.20	0.0	0.0	1.8	1.5	6.2	9.6	15.0	8.5
D_2D_3''	1.23*	0.0	0.0	0.0	0.0	0.0	0.0	<1.0	1.9

TABLE 5.7

Degradation Products (% Weight) at 300°C from Polydimethyl/ /diphenyl Siloxanes

Compound	Rf Value (*Est.)	B	C	G	H
D_3	0.86	<1.0	6.3	0.0	0.0
D_4	0.89	<1.0	3.9	0.0	0.0
D_5	0.91	<1.0	2.8	0.0	0.0
D_6	0.92*	1.0	5.6	0.0	0.0
D_7	0.92*	1.0	9.9	0.0	0.0
D_8	0.92*	<1.0	<1.0	0.0	0.0
D_2D_1''	1.00	22.2	37.6	5.2	2.8
D_9	0.92*	<1.0	3.8	0.0	0.0
D_3D_1''	1.02	6.9	5.9	1.6	1.8
D_4D_1''	1.03*	<1.0	0.0	<1.0	0.0
D_5D_1''	1.04*	2.5	2.4	<1.0	0.0
D_6D_1''	1.04*	2.6	1.6	1.7	1.8
?	1.04*	<1.0	2.8	5.5	0.0
D_3D_1''	1.04*	<1.0	0.0	0.0	0.0
?	1.08*	<1.0	0.0	0.0	0.0
cis D_2D_2''	1.15	15.0	4.1	8.0	7.4
D_1D_2''	1.11	28.2	9.7	30.8	52.6
trans D_2D_2''	1.15	7.9	1.3	6.0	6.1
D_3D_2''	1.17*	2.9	1.2	5.9	<1.0
D_4D_2''	1.19*	2.8	0.0	0.0	0.0
D_1D_3''	1.23*	1.1	0.0	26.7	19.2
D_2D_3''	1.23*	1.3	0.0	8.9	4.6

TABLE 5.8

Relative Amounts of Cyclic Degradation Products from Polydimethyldiphenyl Siloxanes

Copolymer	Total % Weight of Dimethyl Cyclics		Total % Weight of Mixed Cyclics		Total % Weight of Diphenyl Cyclics	
	300°C	500°C	300°C	500°C	300°C	500°C
A	-	18.1	-	81.9	-	0.0
B	3.9	14.2	96.1	85.8	0.0	0.0
C	32.7	6.5	67.3	91.7	0.0	1.8
D	-	3.1	-	95.4	-	1.5
E	-	0.0	-	93.8	-	6.2
F	-	0.0	-	90.4	-	9.6
G	0.0	0.0	100	85.0	0.0	15.0
H	0.0	0.0	100	91.5	0.0	8.5

5.7 Discussion

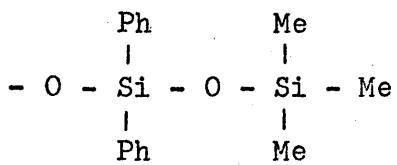
The most obvious features from the TGA data are that increasing the phenyl content of the copolymers increases their stability in terms of the final weight of the residue and the temperature of initial weight loss, whereas end-blocking leads to the copolymers being less stable. Data from TVA again suggests that the temperature of initial degradation increases with phenyl content but that end-blocking of the copolymers gives slightly higher initial degradation temperatures.

The increased stability of copolymers with high phenyl content can be explained by the inductive effect of the phenyl groups. It has been shown (Ref: 36) that electron withdrawing groups on the silicon atom can strengthen the Si-O bond by the increased participation in bonding of the oxygen lone pairs giving it double bond character. Thus the siloxane backbone becomes stronger with increasing phenyl content.

The results of benzene evolution from the Vacuum Line Degradation System at 300^{o}C are again consistent with the hydroxy chain-end mechanism proposed earlier (Section 3.7). Thus, end-blocking the copolymers produces less stable samples, since the chain ends cannot react to form stabilising cross-links at lower temperatures. Copolymer F is more stable than copolymer E although both have the same phenyl content (50%). This is because F has a lower molecular weight than E and so will have more hydroxy chain ends which will consequently form more cross-links.

Thus, F being more cross-linked, will not be able to undergo depolymerisation as readily as E and will, therefore, give a larger residue.

As expected, the amounts of benzene produced at 500°C increase with the phenyl content of the copolymers. Unlike the previous systems studied, however, the end-blocked samples evolve less benzene than their hydroxy ended analogues.This is due to the fact that the phenyl groups at the chain ends are no longer in an electronically unsymmetrical environment i.e.



and are, hence, not labile.

The weight losses at 500°C from the end-blocked samples are greater than those from the hydroxy ended ones since the former do not evolve as much benzene (and so will have fewer cross-links) as their hydroxy ended analogues.

Bicyclic compounds containing methylene bridging groups have again been identified in the degradation products at 500°C suggesting that the mechanism proposed earlier (Section 3.7) for the random evolution of benzene is also occurring in this system.

The distribution of the cyclics produced at 500°C is as expected, with the amounts of mixed dimethyldiphenyl cyclics forming the largest part of the 'cold ring' fraction. No diphenyl cyclics are detected at 300°C because they would undergo secondary rearrangements beforethey could escape from the hot polymer due to their involatility at this temperature.

CHAPTER 6

Comparison of Poly(methylphenyl), Poly (dimethyl/ methylphenyl) and Poly(dimethyldiphenyl) Siloxanes

The thermal stability of the above named polysiloxanes will be compared and the results discussed in terms of the effect of the different distributions of methyl and phenyl groups along the chain.

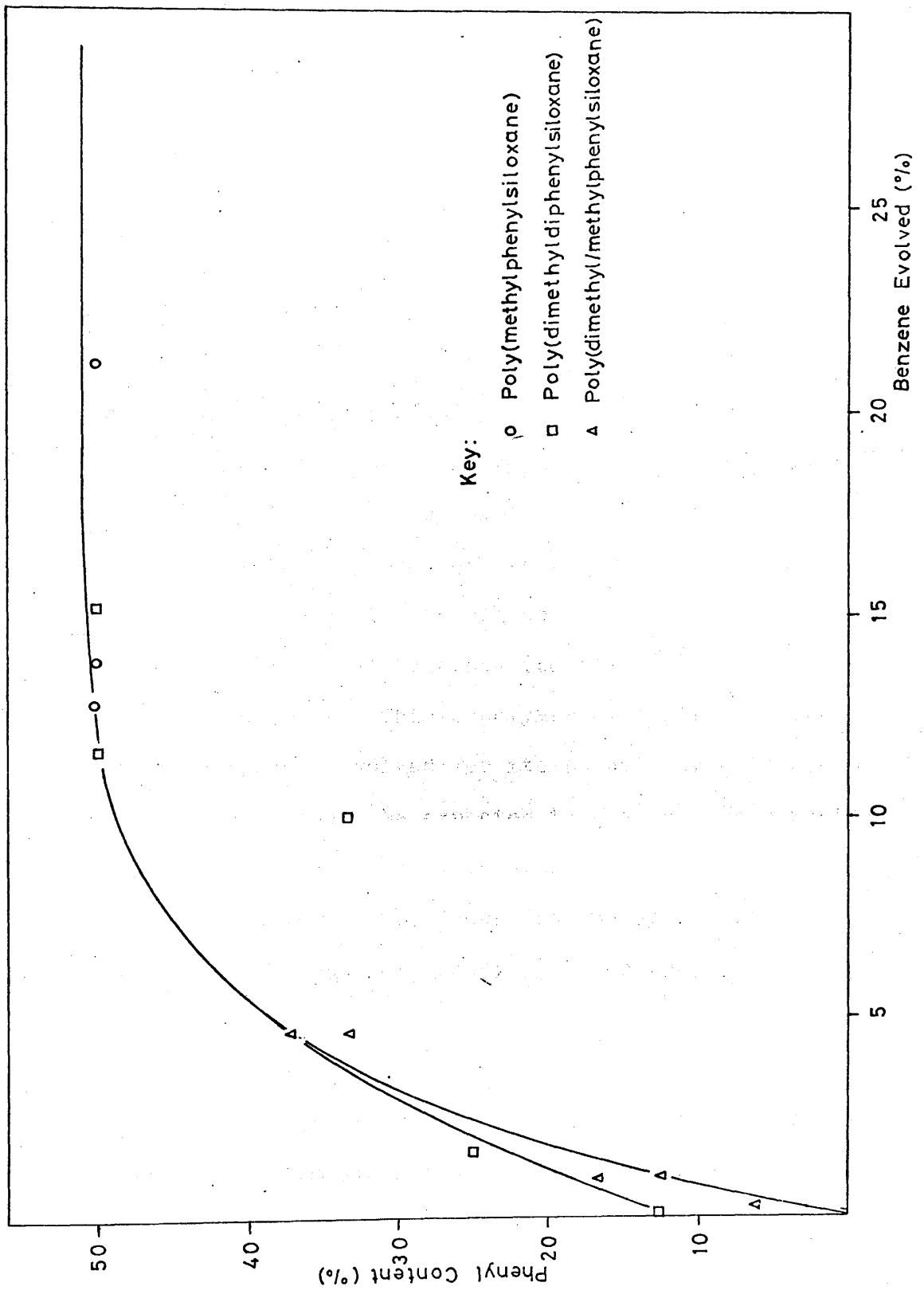
6.1 Evolution of Benzene

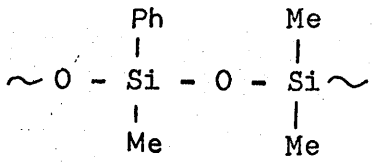
Figure 6.1 shows the percentage of benzene evolved at 500°C versus the percentage phenyl content of the hydroxyl ended polymers. The percentage of benzene evolved is given by dividing the actual amount produced by the amount that would be evolved if every phenyl group in the polymer dissociated to give one molecule of benzene and then multiplying the whole by 100.

The amount of benzene appears to depend only on the phenyl content of the polymers and not the arrangement of phenyl groups, except for polydimethyl/methylphenyl siloxanes with lower methylphenyl content. This confirms earlier work (Refs: 54, 60, 61) that phenyl groups in the following grouping are more labile than otherwise.

FIGURE 6.1

% Benzene Evolved at 500°C vs % Phenyl Content of Methyl and Phenyl Containing Poly Siloxanes (Hydroxy-terminated)





6.2 Isothermal Weight Loss

Data for isothermal weight loss for hydroxy ended polysiloxanes at 500°C are shown on Figure 6.2.

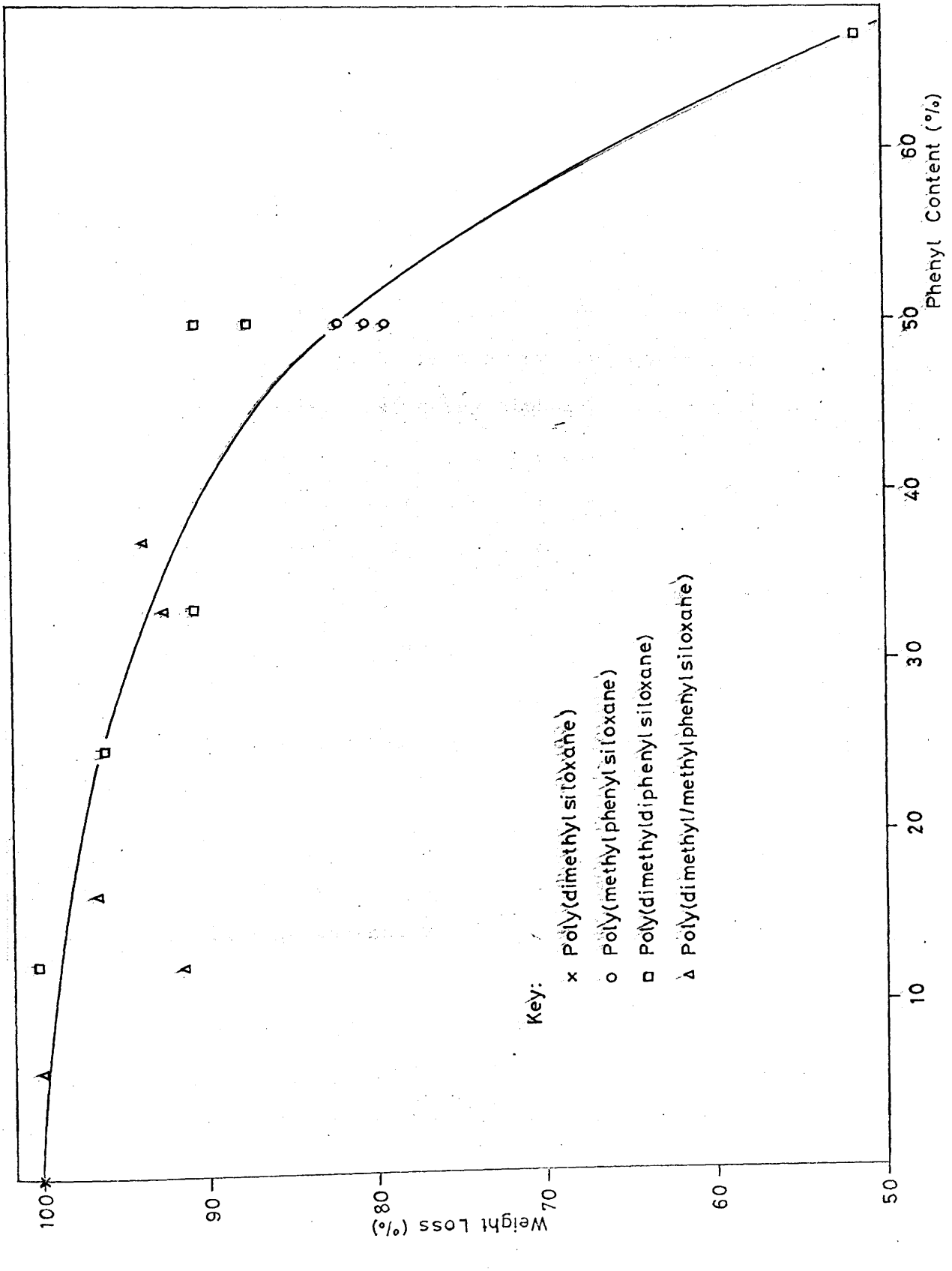
The stability (as measured by the amount of residue after degradation) is seen to increase with the phenyl content of the polymers. The trend in stability appears to depend on the phenyl content and not on the arrangement of the methyl and phenyl units in the polymer, although a polydimethyl/methylphenyl siloxane (copolymer E) shows greater stability than expected. This copolymer also gives a high percentage of benzene evolved for its phenyl content (see Figure 6.1) and so would be expected to have a larger residue due to the greater number of cross-links.

Conclusions which can be drawn from these results must be viewed with some caution, however, since they do not take the effect of varying molecular weight into account.

The effect of molecular weight on weight loss between different polysiloxane systems, can only be judged with polymethylphenyl siloxane and with those polydimethyldiphenyl

FIGURE 6.2

Plot of % Weight Loss at 500°C vs % Phenyl Content of Methyl and Phenyl Containing Polysiloxanes (Hydroxy-terminated)



siloxanes with the same phenyl content(that is, 50%). These data are shown on Figure 6.3.

It is immediately apparent that the polydimethyldiphenyl siloxanes are less stable than the polymethylphenyl polymers. It is thought that this is due to the dimethyl units in the former samples weakening the Si-O bonds by the electron donating effect of the methyl groups (Ref: 36) and, thus leading to larger weight losses. Also, with polymethylphenyl siloxane, the phenyl groups on every silicon atom would sterically hinder the close approach of the chains which is necessary for inter and intra-molecular rearrangements which lead to the production of cyclics and subsequent weight loss. With polydimethyldiphenyl siloxane, however, the smaller dimethyl units would allow the chains to approach each other more closely at regular intervals along the polymer backbone.

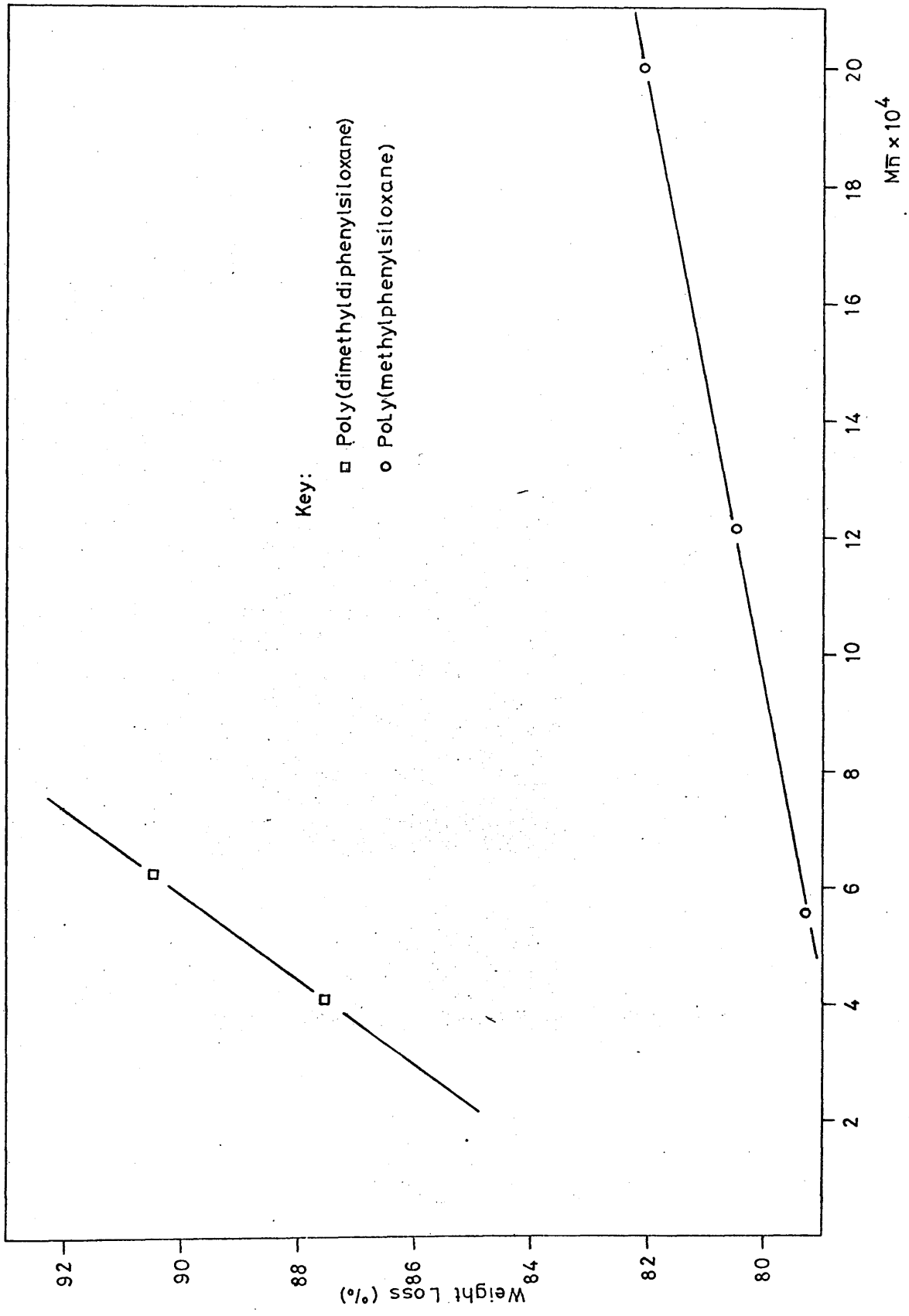
6.3 Suggestions for Future Work

As has been suggested above, the study of polysiloxanes with the same percentage phenyl content and molecular weight but with different methyl and phenyl arrangements in the polymer chain, would be necessary for the effect of structure on thermal stability to be properly understood.

^{29}Si NMR has been shown by various workers (Refs: 70, 71 and 72) to be of great potential for the determination of the microstructure of polysiloxanes. This technique would be invaluable for the study of changes taking place

FIGURE 6.3

% Weight Loss (500°C) from Hydroxy-terminated Polysiloxanes with 50% Phenyl Content vs Molecular Weight



during the degradation of these polymers as well as elucidating the mechanism of polymerisation.

The preparation and study of polymethylphenyl/diphenyl siloxanes would complete all the possible different arrangements of methyl and phenyl units in these linear copolymer systems.

CHAPTER 7

Poly(Siloxane-Urethane) Copolymers

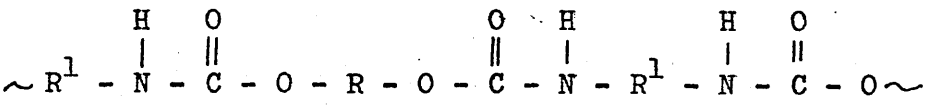
7.1 Introduction

A - Polyurethanes

Diisocyanates have become important starting materials for the production of polyurethanes due to their ability to react readily with such compounds as glycols, amines, amides, esters and carboxylic acids (Ref: 70).

Preliminary research was carried out on the condensation reaction of diisocyanates with diamines which produced polyureas. These compounds were infusible and hydrophilic, however, and were of little commercial use although they did possess good thermal properties. Bayer (Ref: 71), in 1947, was the first to react a diisocyanate with a glycol which is now the general method of producing polyurethanes.

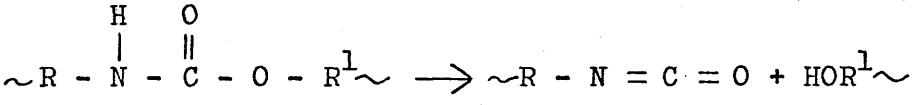
The general structure of polyurethanes is represented by



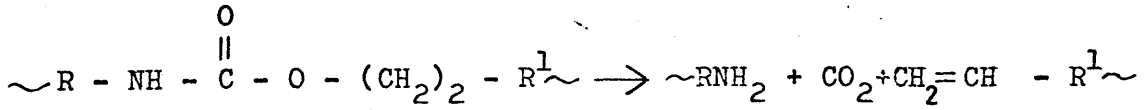
The properties of the polymer are greatly influenced by the choice of R and R^1 groups. The use of aryl diisocyanates, for example, gives more rigid samples whereas more flexible materials would be formed when long $-(CH_2)_x-$ chains are present. Polyurethanes have found uses as fibres, paints, adhesives and surface coatings. Foams may also be prepared by using the side reaction of water with isocyanates to liberate carbon dioxide.

The degradation of organic polyurethanes has been studied by a number of workers (Refs: 72-75) and their results may be explained in terms of the following three main depolymerisation reactions.

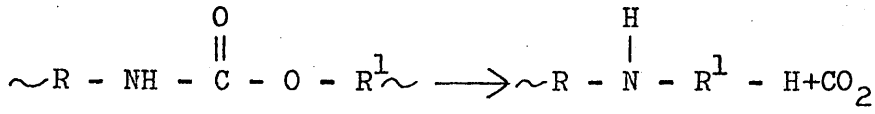
(i) The reverse of the polymerisation to form isocyanate and alcohol



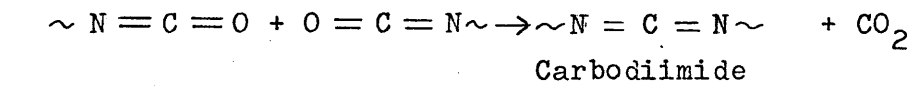
(ii) Dissociation to give amine, olefin and CO_2

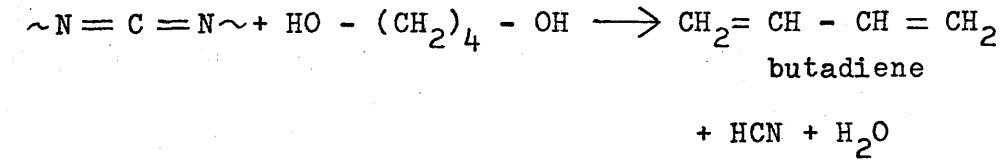


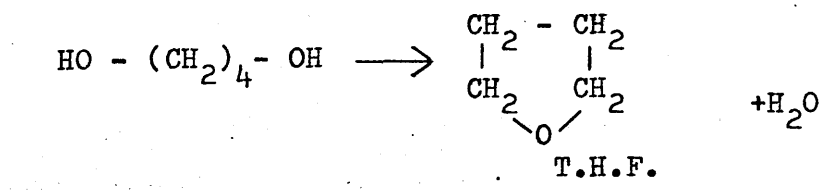
(iii) Dissociation to give a secondary amine and CO_2



More recently, Grassie and Zulfiqar (Ref: 76) studying the thermal behaviour of a polymer based on 4,4' - diphenylmethane diisocyanate (M.D.I.) and 1,4 - butane diol, have shown that reaction (i) is the most likely and is followed by a number of secondary reactions.

a) 

b) 

c) 

d) $\sim N = C = O + H_2O \longrightarrow \sim NH_2 + CO_2$

B Polysiloxanes

These polymers have been discussed in earlier Chapters.

C Poly (siloxane-urethane) copolymers

Although both siloxanes and urethanes have been extensively studied, the literature contains surprisingly few references to the formation of an $-\overset{|}{\underset{|}{Si}}-O-CONH-$ linkage.

Bryk et al (ref: 77) have prepared a siloxane-urethane copolymer by condensing an $\alpha - \omega$ polysiloxane diol (mol. wt. $\sim$ 800) with an $\alpha - \omega$ macrodiisocyanate (mol. wt. $\sim$4000). These workers only studied the kinetics of the reaction and they made no mention of the stability of the final polymer.

Andrianov et al (Ref: 78) polymerised Cl CO_2 $(CH_2)_2$. $(Si\ Me_2\ O)_2$ Si Me_2. CH_2 O $(CH_2)_2$ CO_2 Cl with NH_2 $(CH_2)_6$ NH_2 and with p - Ph $(NH_2)_2$, in the presence of HCl in an organic solvent. This reaction gave copolymers with very good heat resistance.

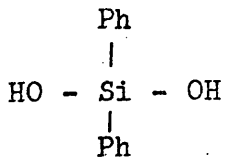
Petrovic (Ref: 79) has prepared a siloxane based urethane by reacting an $\alpha - \omega$ polydimethylsiloxane diol (mol. wt. 900) with M.D.I. in bulk. He claimed that the reaction occurred readily with good conversion to copolymer but that the siloxane-urethane link had very low hydrolytic stability, due to the ionic nature of the bond. However, the thermal stability of the copolymer was shown to be better than that of organic urethanes.

More recently Sedova et al (Ref: 80) have prepared polysiloxane-urethanes for use as optical adhesives which have, the authors claim, high light transmission and high resistance to both moisture and shrinkage.

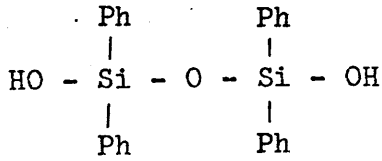
Work described in this chapter will relate to the preparation of a series of $\alpha - \omega$ siloxane diols, containing one to three silicon atoms, and their attempted copolymer/isation with M.D.I. The thermal stability of the polysiloxane-urethane copolymers which can be prepared, will then be compared with each other and with that of organic urethanes.

7.2 Preparation of Monomers

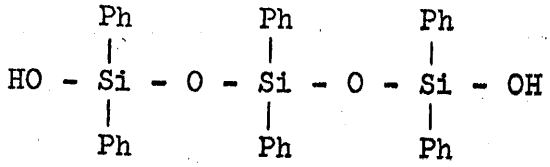
The following $\alpha - \omega$ siloxane diols were isolated as described in Chapter 2.



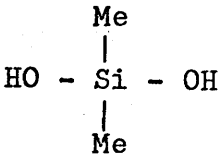
Diphenyl diol



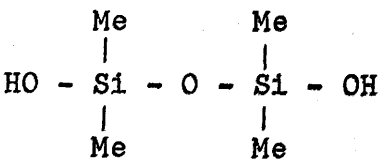
Tetraphenyl diol



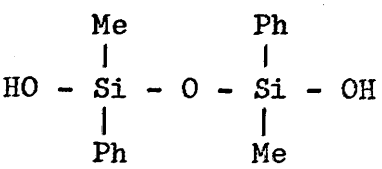
Hexaphenyl diol



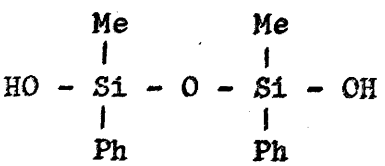
Dimethyl diol



Tetramethyl diol



Dimethyldiphenyl diol
(racemic)



Dimethyldiphenyl diol
(meso)

The diisocyanate, OCN - O - CH_2 - O - NCO, 4,4' diphenylmethane diisocyanate (M.D.I.) was purified by vacuum distillation (120°C/24 mmHg) and stored in the dark under vacuum to prevent decomposition.

7.3 Preparation of Copolymers

The copolymers were prepared by the method described earlier. Table 7.1 gives details of the monomers used and the IR characterisation data.

All attempts to prepare copolymers from dimethyl diols, both in solution (dimethyl-formamide and toluene) and in bulk were unsuccessful. IR spectra of the products formed by the reaction of the dimethyl diols with MDI, were identical to the spectrum of the product prepared by condensing MDI with water, that is a polyurea (Figure 7.1).

Figure 7.2 shows the IR spectrum (KBr disc) of a typical polysiloxane-urethane (copolymer A).

The samples prepared were white crystalline powders and were insoluble in all common solvents. Their hydrolytic stability appeared to be good - there was no noticeable difference in the urethane bands in the IR spectra when the copolymers were shaken with water for thirty minutes. Dissolution of the copolymers in dimethyl-formamide, however, resulted in the hyrolysis of the urethane linkage.

The IR spectra of all the copolymers shows evidence of the formation of urea linkages (around 1650 cm^{-1}). It is thought that this is due to the partial condensation of the siloxane diols with the formation of water which can then react with the isocyanate to form urea.

TABLE 7.1

Preparation of Poly(siloxane-urethanes)

Copolymer	Starting Material	Characteristic IR Bands		
		Urethane $1700-1720 cm^{-1}$	Urea $1640 cm^{-1}$	Isocyanate $2250-2275 cm^{-1}$
A	Diphenyl diol	✓	✓	✓
B	Tetraphenyl diol	✓	✓	✓
C	Hexaphenyl diol	✓	✓	✓
D	Dimethyldiphenyl diol	✓	✓	✓
E	Dimethyl diol	Absent	✓	✓
F	Tetramethyl diol	Absent	✓	✓
G	Water	Absent	✓	Absent

FIGURE 7.1

IR Spectrum of Copolymer G (Polyurea)

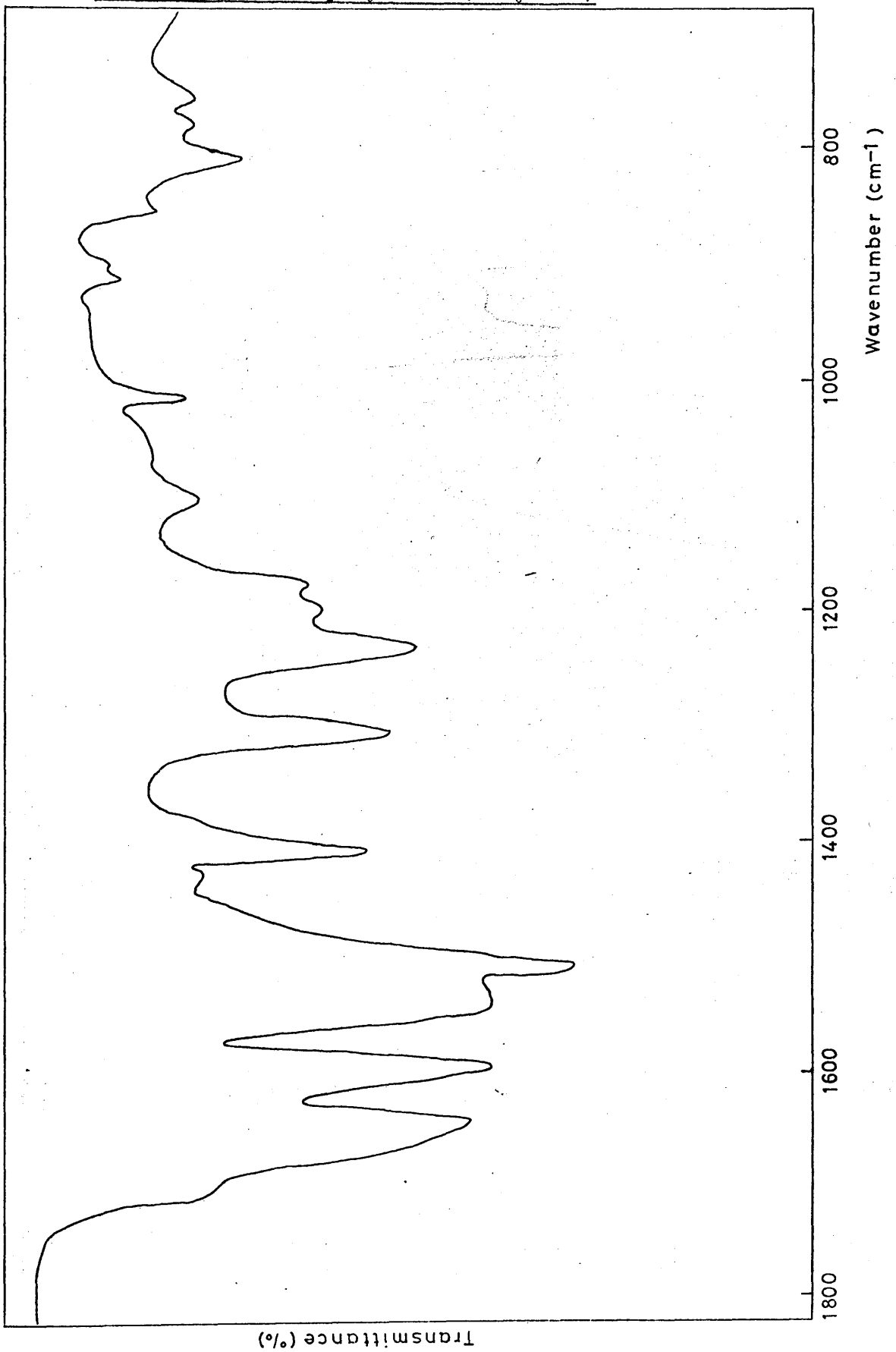
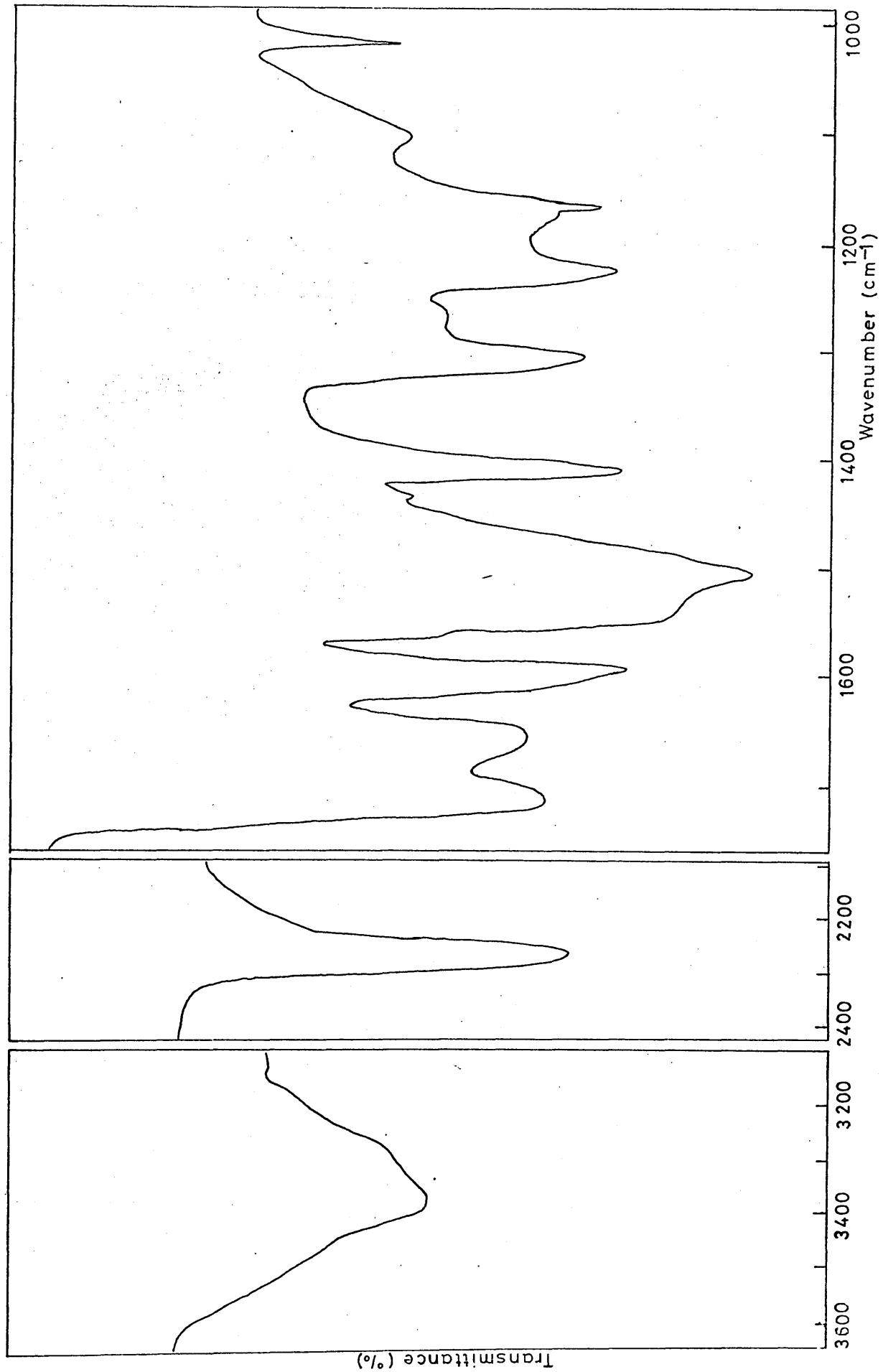


FIGURE 7.2

IR Spectrum of Copolymer A



7.4 T.G.A.

Figure 7.3 shows the TGA traces for copolymers A and G (polyurea). The polyurea undergoes weight loss at two distinct stages - at around 375°C and 580°C - whereas the polysiloxane-urethane shows weight losses at 250°C as well as at about 375°C and 580°C.

7.5 T.V.A.

TVA traces of the polysiloxane-urethane copolymers (A, B, C and D) and the polyurea (G) are shown on Figure 7.4.

The 0°C, -45°C, -75°C and -100°C traces are co-incident in all cases and there is no evidence of the production of any products non-condensable at -196°C. A, B, C and D all have twin peaks in the 200°C - 320°C region and they evolve more volatiles towards the end of the programmed TVA run whereas G (the polyurea) has only one peak at 349°C.

Analysis of degradation Products

i) Condensable volatiles

The condensable volatiles were distilled into a gas cell and IR spectra were recorded. In every case, peaks were observed at 2310, 715 and 660 cm^{-1} which are characteristic of carbon dioxide.

Benzene was also identified in the products from A, B, C and D by UV spectroscopy (Figure 7.5).

FIGURE 7.3

TGA Trace of a Polyurea and a Polysiloxane-Urethane

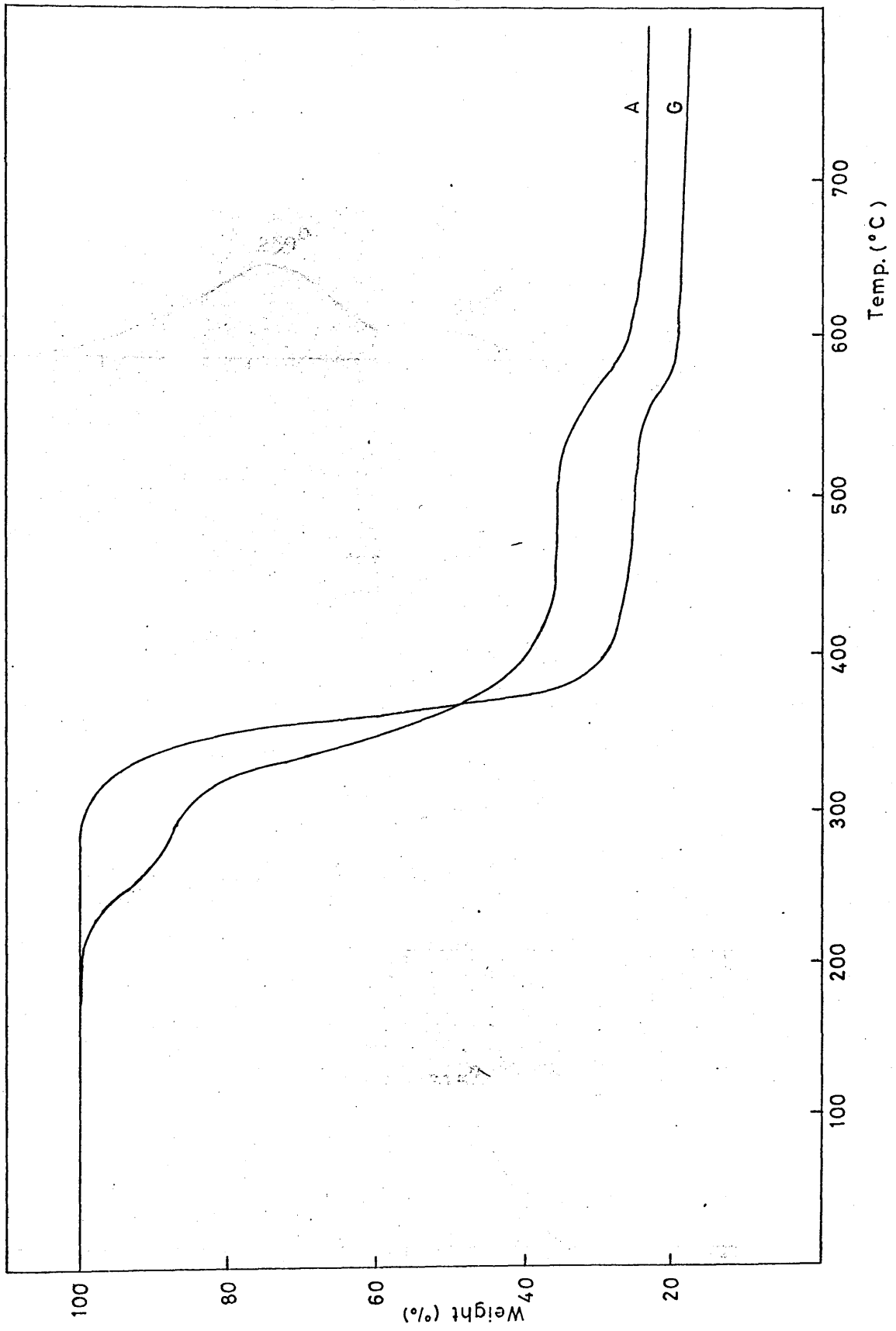


FIGURE 7.4

TVA Traces of Polysiloxane-urethanes

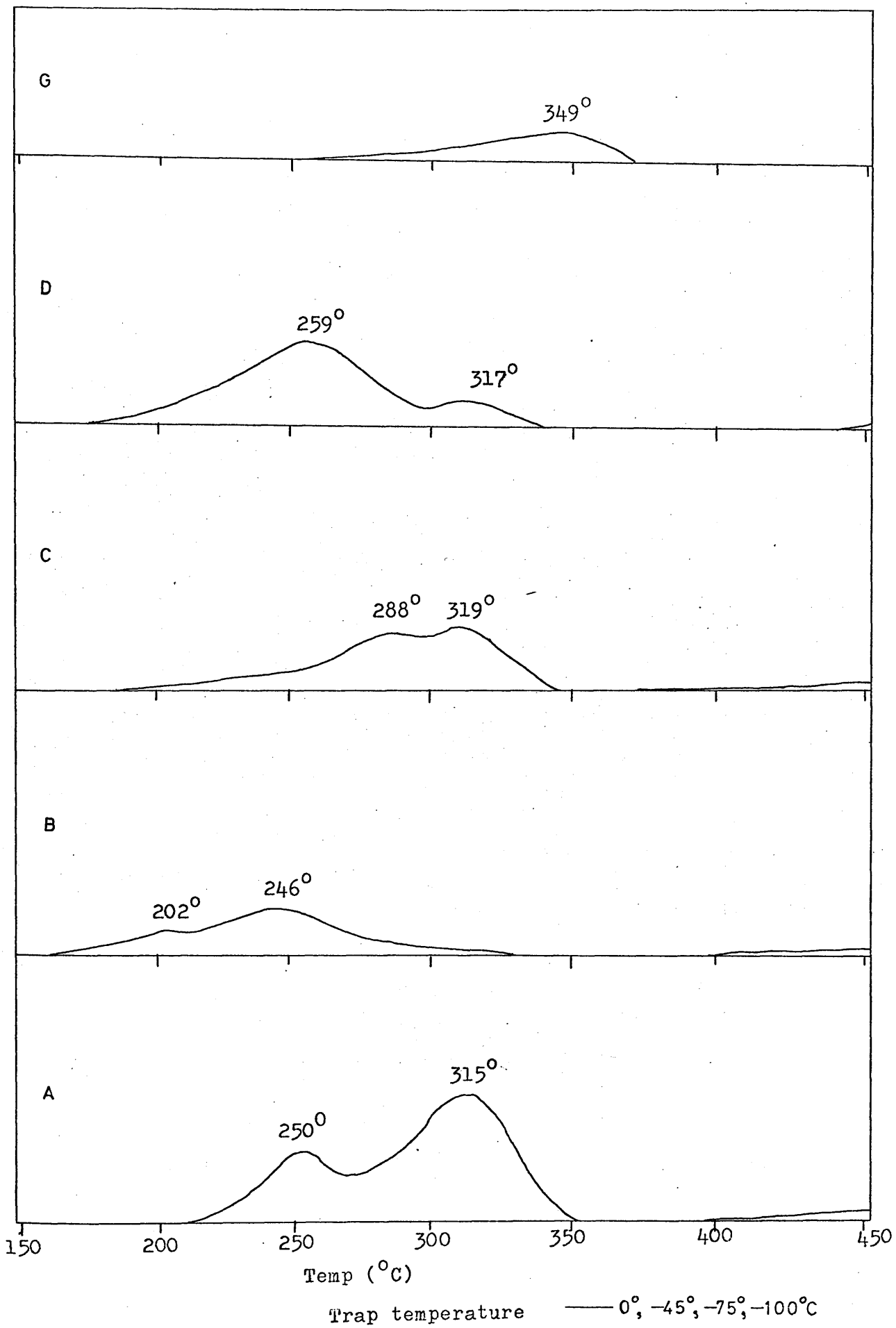
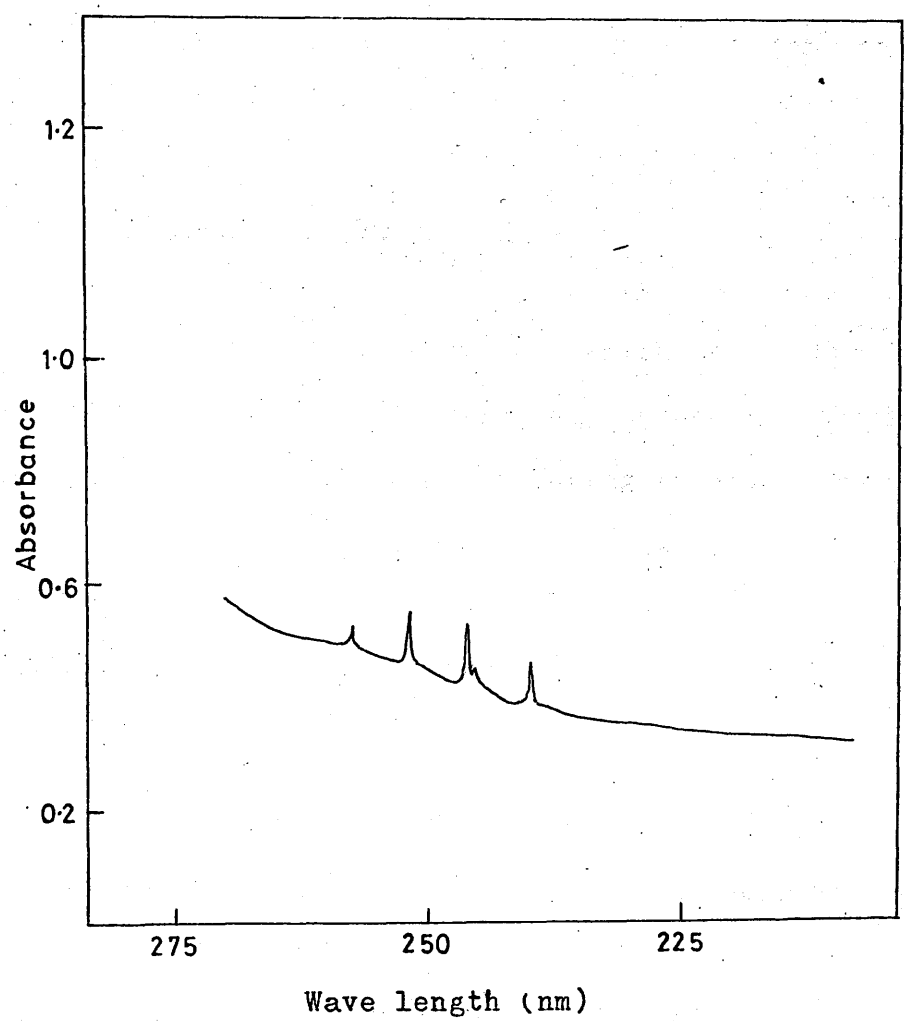


FIGURE 7.5

UV Spectrum of Condensable Volatiles from TVA of Polysiloxane-urethanes



ii) Cold ring fraction

IR spectra of the cold ring fractions were run as KBr discs as no suitable solvents could be found. Figure 7.6 illustrates the IR spectrum of the cold ring fraction from copolymer A. The urethane band (1710 cm^{-1}) has almost totally disappeared but all the other bands seen in the unde graded copolymer, are still present. The peaks at 2120 and 2100 cm^{-1} are the only new peaks seen and thesecan be assigned to the carbodiimide structure (Ref: 81).

iii) Polymer residue

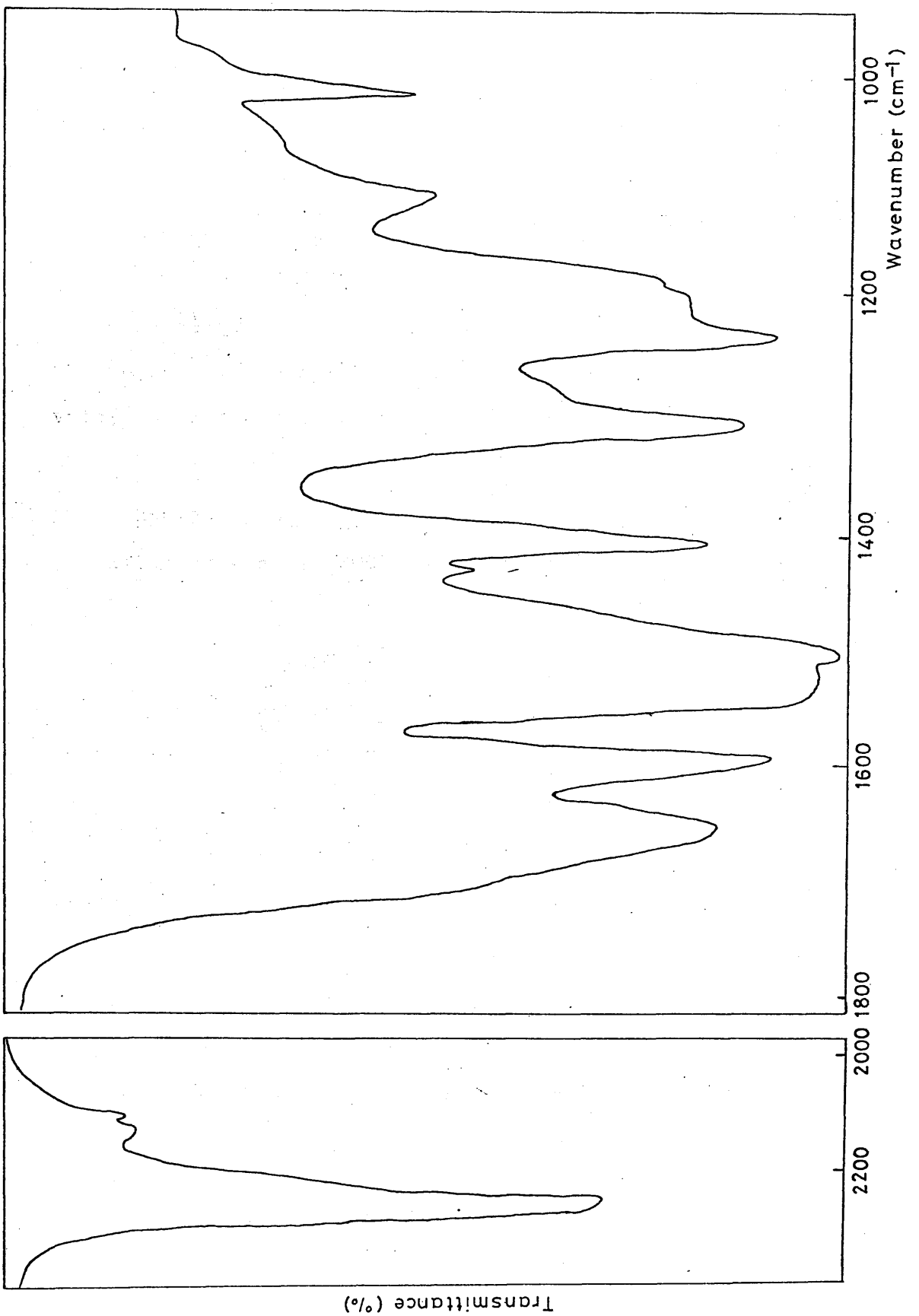
IR spectra of the residues, which were brown in colour, were run as KBr discs and showed the complete disappearance of all bands relating to urea, urethane, isocyanate and carbodiimide. In the poorly resolved spectra, the only bands remaining corresponded to the siloxane part of the copolymer.

7.6 Isothermal Degradation

A sample of copolymer D was heated under vacuum to 200°C, 260°C, 320°C and finally to 500°C and held at each temperature for thirty minutes. After each heating cycle, the copolymer was cooled to ambient temperature and a sample was removed for IR analysis (KBr disc). The spectra obtained at each temperature were compared to

FIGURE 7.6

IR Spectrum of TVA Cold Ring Fraction from Copolymer A



that of the original sample (Figure 7.7). The volatile products evolved at the various temperatures were collected and analysed in the gas phase by IR and UV spectroscopy.

Analysis of degradation products

(i) Volatiles

Table 7.2 shows the analytical results for the volatiles collected at each temperature.

(ii) Residual polymer

After heating at 200°C for thirty minutes, the urethane band (1710 cm^{-1}) became smaller relative to the urea band at 1650 cm^{-1}. The isocyanate band also became less intense.

Degradation at 260°C leads to the disappearance of the urethane band and to the formation of twin peaks at 2120 and 2100 cm^{-1} which are due to the carbodiimide group.

The carbodiimide bands, although less intense, are still seen after heating to 320°C but all the urea and urethane bands have almost totally disappeared.

At 500°C, the carbodiimide bands have disappeared leaving only those due to the siloxane structures.

FIGURE 7.7

IR Spectra of Copolymer D (Isothermally Degraded)

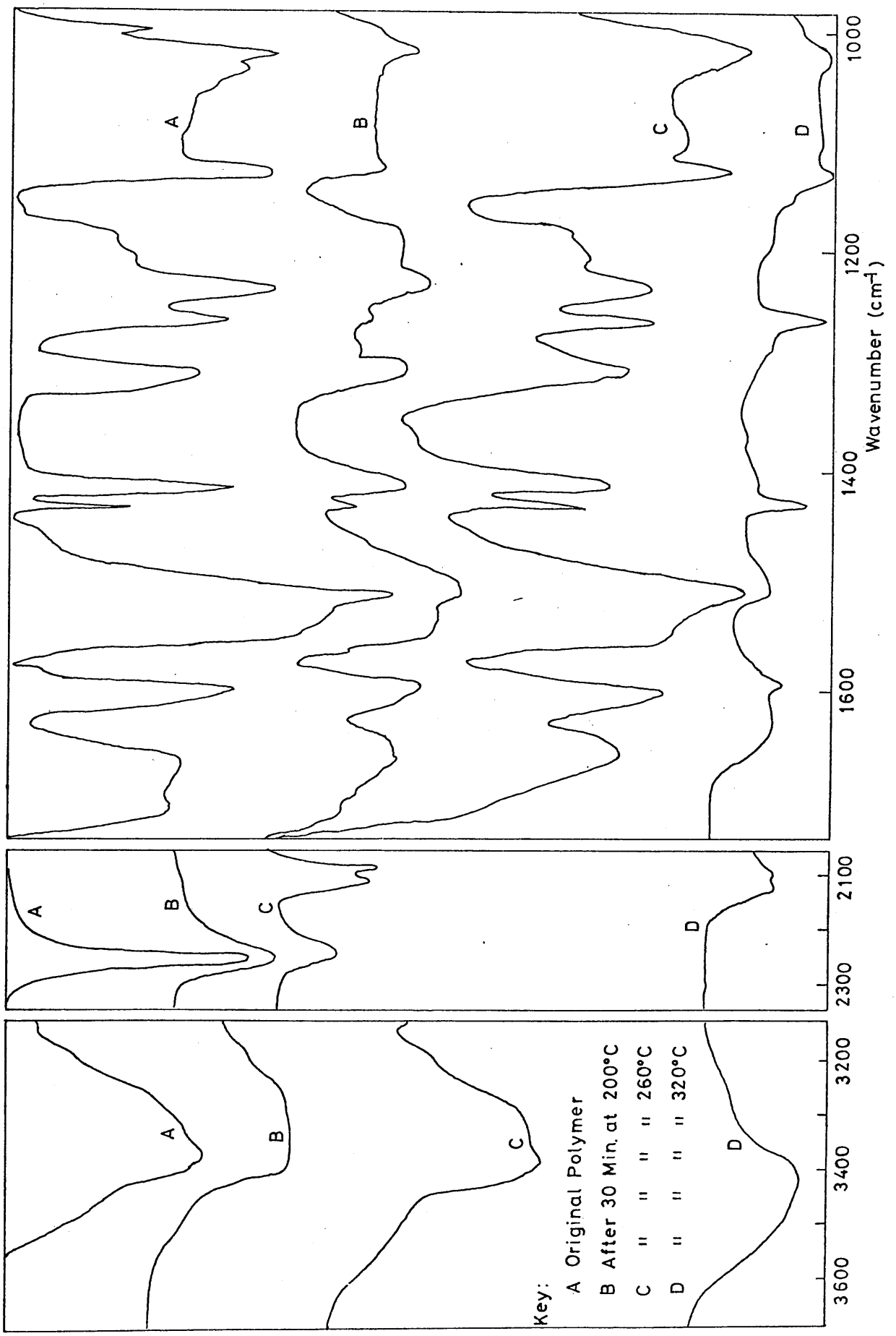


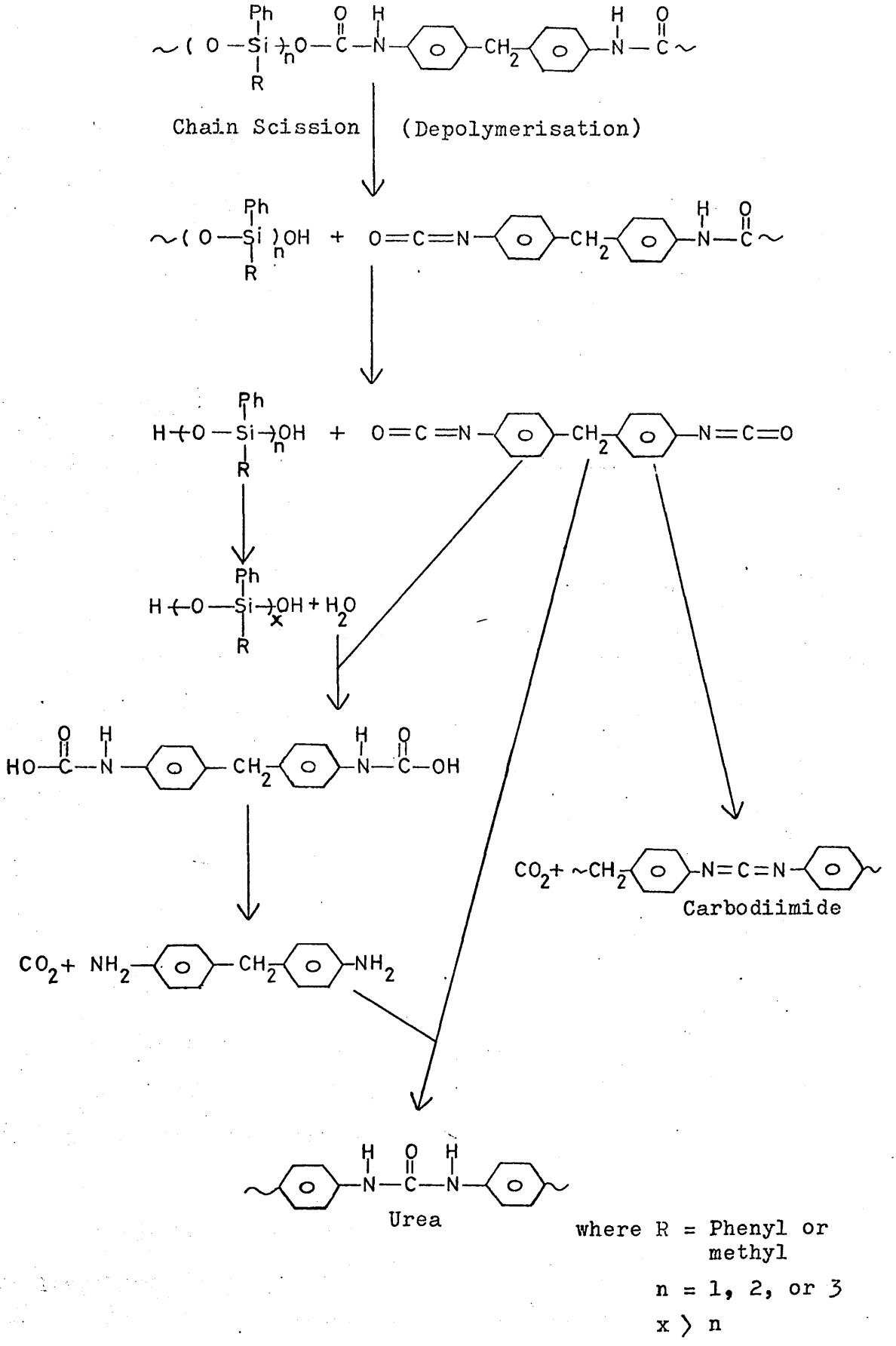
TABLE 7.2

Volatile Products Formed from Isothermal Degradation of Copolymer D

Temperature (^{o}C)	Products Formed
200	CO_2
260	CO_2
320	None
500	C_6H_6

7.7 Discussion

Comparison of data from TGA, TVA and isothermal degradations suggests that the urethane linkage is less stable than the urea bond but that both decompose with the evolution of carbon dioxide. Grassie and Zulfiqar (Ref: 76) have shown that the primary degradation reaction in organic polyurethanes is depolymerisation with formation of alcohol and isocyanate. These groups then undergo secondary reactions to form, amongst other products, carbon dioxide, carbodiimide and ureas. Since these products are also produced by the degradation of polysiloxane-urethane copolymers, it is proposed that the decomposition of these copolymers follows a similar mechanism to that suggested for organic urethanes (Ref: 76):-



where R = Phenyl or methyl

n = 1, 2, or 3

x > n

Unlike organic urethanes, the 'alcohol' part of the polymer does not undergo secondary degradation reactions. Under TVA conditions, only benzene, which is formed via the scission of the Si-Phenyl bonds,is seen as a degradation product from the siloxane part of the copolymer. Siloxane cyclics, which would be expected, if scission of the Si-O bonds was occurring, are not present in the decomposition products.It is thought that this is due to the decreased mobility of the chains - caused by cross-linking of the urea residues - preventing the siloxane bonds from rearranging into cyclic siloxanes.

Comparison of the stability of these copolymers with the polyurethane prepared from butane 1,4 diol and MDI, showed the latter to be more stable by about 50°C. This difference is probably due to the ionic nature of the siloxane-urethane band, which is caused by the low electonegativity of silicon, weakening the bond.

7.8 Suggestions for Future work

The preparation of pure copolymer samples, either by the prevention of urea formation or by its separation from the siloxane-urethane copolymer, would be advantageous for a better understanding of the properties of the copolymer system.

A more thorough investigation of the effects of the length of the siloxane unit and the types of organic groups attached to the silicon atoms would also be desirable, as would changing the diisocyanate used.

For the commercial assessment of this copolymer, a more thorough study of its physical properties would be vital.

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